Explicit solvent theory of salt-induced dielectric decrement†

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We introduce a field-theoretic electrolyte model composed of structured solvent molecules and salt ions coupled by electrostatic and hard-core (HC) interactions. Within this explicit solvent framework, we characterize the salt-driven dielectric decrement by including salt–solvent correlations beyond weak-coupling (WC) electrostatics. The WC approximation of prior formalisms is relaxed by treating the salt charges via a virial expansion. This virial approach enables the explicit inclusion of the many-body salt–solvent interactions, and directly leads to the experimentally observed linear decay of the electrolyte permittivity with added dilute salt. The permittivity formula emerging from our approach indicates that the reduction of the solvent permittivity is induced by the salt screening of the polarization charges suppressing the dielectric response of the solvent. By comparison with experiments, we also show that the salt-dressed permittivity formula can equally reproduce the attenuation of the electrolyte permittivity with rising temperature, the thermal decay of the dielectric decrement, and its intensification with the salt valency. In accordance with the observation of previous numerical simulations and implicit solvent theories, the consistent qualitative agreement of our theory with this wide range of experimental trends points out the electrostatic ion–solvent correlations as the primary mechanism behind the salt-induced dielectric decrement.

I. Introduction

The process of salt solvation in water is a vital regulator of biological processes sustaining life on earth. By preventing oppositely charged ions from forming neutral pairs, solvation acts as a key mediator for the salt-induced regulation of various mechanisms ranging from the stability of DNA molecules around histones to nanofluidic charge transport through ion channels in the cell medium.1–3 This universal role implies that the accurate characterization of solvation is an essential step to decipher the functioning of living organisms.

Ionic solvation originates from the dielectric screening of the mobile charges by the strongly dipolar water molecules. Within the framework of solvent-implicit electrostatics, the strength of this effect is characterized by the macroscopic dielectric permittivity setting the magnitude of the pairwise electrostatic interactions. The first limitation of the implicit solvent electrostatics is the uniformity of the dielectric permittivity, which is contradicted by AFM experiments4 and MD simulations5,6 indicating the spatially inhomogeneous dielectric response of polar solvents around charge sources.

With the aim to account for the non-uniformity of the hydration by water, earlier non-local electrostatic formalisms integrated structured dielectric permittivities into the electrostatic equations of state.7,8 By generalizing the point-dipole model of ref. 9 and 10 to solvent molecules with finite size, we introduced the first field-theoretic formulation of non-local electrostatics able to map from the intramolecular solvent structure to inhomogeneous dielectric response.11,12 In these works, we showed that the consideration of the extended charge structure of solvent molecules directly leads to the structured dielectric permittivity profiles13 observed in AFM experiments5 and explicit solvent simulations.5,6

An additional limitation of the solvent-implicit electrostatics is the experimentally confirmed inconsistency of the hierarchy between the salt-driven Debye screening and the solvent-induced dielectric screening. Namely, in the implicit solvent formulation of electrolyte solutions, the strength of the salt screening quantified by the Debye–Hückel (DH) parameter depends on the dielectric permittivity of the liquid, whereas the liquid permittivity is assumed to be independent of the salt concentration.

The inaccuracy of this assumption has been demonstrated by the experimental observation of dielectric decrement upon salt addition into water. Over the past six decades, various characteristics of this effect have been probed by a wide range of experiments. The common observation of these experiments can be mentioned as the linear decay of the dielectric permittivity with added dilute salt and the transition to a non-linear decrement regime at molar salt concentrations, the reduction

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of the electrolyte permittivity with rising temperature, and the amplification of the dielectric decrement with the valency of the salt ions.\textsuperscript{14–25}

Owing to the complexity of the non-local electrostatics, salt-induced dielectric decrement has been mainly investigated by implicit solvent theories and numerical simulations. Namely, the effect of the salt-dependent permittivity on the activity coefficient of NaCl solutions has been considered by Valisko\'e and Boda \textit{via} solvent-implicit simulations.\textsuperscript{26} By comparison with experiments, Saric \textit{et al.} studied the dielectric decrement by explicit solvent simulations.\textsuperscript{27} The problem has been equally analyzed \textit{via} a microfield approach,\textsuperscript{28} the dressed-ion theory,\textsuperscript{29} the Booth equation,\textsuperscript{30} the Ornstein–Zernick formalism,\textsuperscript{31} generalized Debye–Langevin models,\textsuperscript{32,33} and a lattice Monte-Carlo approach.\textsuperscript{34} \textit{Via} quantum \textit{ab initio} and classical simulations, Self \textit{et al.} explained as well the experimental observation of dielectric increment in low permittivity liquids in terms of ionic pair formation.\textsuperscript{35}

The consistent characterization of the dielectric decrement effect involving salt and solvent molecules on an equal footing requires the investigation of the problem by an explicit solvent framework. Prior solvent-explicit field-theoretic approaches showed that the WC treatment of purely electrostatic models does not capture the salt-driven dielectric decrement. Indeed, within the framework of a point-dipole model, the calculation of the electrolyte permittivity \textit{via} a one-loop-level WC approach was shown to yield the Debye–Langevin relation corresponding to the pure solvent permittivity.\textsuperscript{36,37} Moreover, our Gaussian-level WC analysis of the field-theoretic solvent model of ref. 11 led to an identical result.\textsuperscript{12} Subsequently, Adar \textit{et al.} showed that the incorporation of the excluded-volume effects to the liquid model of ref. 36 and 37 generates the effect of dielectric decrement by salt addition.\textsuperscript{38}

With the aim to carry out the first analysis of the salt-induced dielectric decrement beyond WC electrostatics, we introduce a field-theoretic model of explicit solvent molecules and salt charges coupled by electrostatic and HC interactions. In the evaluation of the field-theoretic partition function, the solvent–solvent interactions are treated within a WC-level Gaussian closure, but the salt–solvent correlations driving the dielectric decrement are included \textit{via} a virial approximation free of any assumption on the strength of the electrostatic coupling. The corresponding extension beyond the WC regime is presented in Section 2. Our strategy is inspired by the hybrid perturbative treatment of solvent-implicit electrolyte mixtures introduced by Kanduc \textit{et al.} and extended by us to analyze correlation effects in nanofluidic charge transport\textsuperscript{41} and polymer translocation.\textsuperscript{42} Namely, by exploiting the strong contrast between the salt and solvent concentrations, we incorporate the salt fluctuations \textit{via} a virial expansion. This virial treatment limits the formalism to moderate salt concentrations but enables the explicit inclusion of the salt–solvent correlations truncated by the WC approximations of the aforementioned works. \textit{Via} the solution of the electrostatic Schwinger–Dyson (SD) equation, we show that this improvement directly gives rise to an electrolyte permittivity linearly decaying with the salt concentration.

In Section 3, we confront this theoretical result with experimental permittivity data and show that our formalism can equally capture the experimentally observed reduction of the electrolyte permittivity with the rise of the temperature, the thermal decay of the dielectric decrement, and its enhancement with the salt valency. We also carry out a detailed analysis of the salt effects on the spatially non-uniform macroscopic dielectric permittivity profile. We show that salt–solvent correlations reducing the magnitude and the range of the dielectric screening also suppress the non-locality of the electrostatic interactions by smoothing the dielectric permittivity structure in the vicinity of charge sources. The limitations of the model and possible extensions are elaborated in Conclusions.

II. Explicit solvent formalism

A. Derivation of the field-theoretic partition function

We introduce here our electrolyte model depicted in Fig. 1. The electrolyte is composed of dipolar solvent molecules and \textit{p} species of point-like salt ions. Each ion of the species \textit{j} has valency \(q_j\), fugacity \(A_j\), and concentration \(\rho_j\). Moreover, the solvent dipoles of size \(a\), fugacity \(A_w\), and liquid water concentration \(\rho_w = 55\text{ M}\) carry the terminal charges \(\pm Q = \pm 1\).

Each solvent molecule or salt particle is placed inside an impenetrable hard-core (HC) sphere of diameter \(d > a\). The center of this sphere coincides with the center of mass (C.M.) of the enclosed molecule. Thus, the pairwise HC interactions between the molecules are mediated by the potential \(v_2(r)\) defined as

\[
e^{-v_2(r)} = H(r - d),
\]

where \(H(x)\) stands for the Heaviside step function. Moreover, the electrostatic interactions between all charges are mediated by the Coulomb potential \(v_e(r) = \epsilon(r)\) including the Bjerrum length \(\ell_B = e^2/(4\pi\epsilon_0 k_B T)\) in vacuum, with the electron charge \(e\), the Boltzmann constant \(k_B\), the ambient temperature \(T\) and the vacuum permittivity \(\epsilon_0\). In the present work, the

![Fig. 1. Schematic depiction of the charged liquid. The liquid is composed of dipolar solvent molecules with size \(a = 1\text{ Å}\) and concentration \(\rho_w = 55\text{ M}\), and \(p\) species of monopolar salt ions. The ionic species \(j\) has valency \(q_j\) and concentration \(\rho_j\) with \(1 \leq j \leq p\). Each salt ion or solvent dipole is confined to a HC sphere with diameter \(d > a\) whose center coincides with the C.M. of the enclosed particle.](image-url)
dielectric permittivities are expressed in units of the vacuum permittivity $\varepsilon_0$.

The canonical partition function of the liquid reads
\[
Z_c = \prod_{j=1}^{N_w} \frac{d^3 \Omega_d}{4\pi} \int d^3 u \prod_{j=1}^{N_l} \int d^3 v_j e^{-\beta(E - \epsilon)},
\]
(2)
with the number of solvent molecules $N_w$, the C.M. position $u_i$ of the dipole $i$, the number of ions $N_l$ of the species $j$, and the C.M. position $v_{jk}$ of the ion with number $k$ in the species $j$. Moreover, the total energy in eqn (2) reads $E = E_c + E_h + E_n$, where we defined the electrostatic, HC, and steric energy components as
\[
\beta E_c = \frac{1}{2} \int d^3 r' d^3 r \hat{\rho}_c(r) \hat{\rho}_c(r') = \frac{1}{2} \int d^3 r' d^3 r \hat{\rho}_c(r) \hat{\rho}_c(r'),
\]
(3)
\[
\beta E_h = \frac{1}{2} \int d^3 r' d^3 r \hat{\rho}_h(r) \hat{\rho}_h(r') = \frac{1}{2} \int d^3 r' d^3 r \hat{\rho}_h(r) \hat{\rho}_h(r'),
\]
(4)
\[
\beta E_n = \sum_{i=1}^{N_w} \hat{\rho}_n(u_i, a_i) + \sum_{j=1}^{N_l} \sum_{k=1}^{N_j} \hat{\rho}_n(v_{jk}),
\]
(5)
respectively.

In eqn (3) and (4), the charge and number density operators are respectively defined as
\[
\hat{\rho}_c(r) = Q \sum_{i=1}^{N_w} \left[ \delta^3 \left( r - u_i - \frac{a_i}{2} \right) - \delta^3 \left( r - u_i + \frac{a_i}{2} \right) \right] + \sum_{j=1}^{N_l} \sum_{k=1}^{N_j} q_j \delta^3 (r - v_{jk}),
\]
(6)
\[
\hat{\rho}_h(r) = \sum_{i=1}^{N_w} \delta^3 (r - u_i) + \sum_{j=1}^{N_l} \sum_{k=1}^{N_j} \delta^3 (r - v_{jk}).
\]
(7)
In addition, the functions $\hat{\rho}_n(u_i, a_i)$ and $\hat{\rho}_n(v_{jk})$ in eqn (5) are the onsite potentials acting on the solvent molecules and the ions, respectively. These one-body potentials will enable us to relate the average density of the particles to their bulk fugacity and concentration. Finally, in eqn (2), the self energy of the particles subtracted from the total energy $E$ is $\epsilon = N_w \epsilon_w + \sum_j N_l \epsilon_j$, with the self-energy components of the solvent molecules and salt ions given by $\beta \epsilon_w = \epsilon_w(0)/2 + Q^2 [v_c(0) - v_c(0)]$ and $\beta \epsilon_j = \epsilon_j(0) + q_j^2 \epsilon_j(0)]/2$, respectively.

At this point, in eqn (2), we introduce an Hubbard–Strattonovitch transformation for each type of pairwise interaction,
\[
e^{-\frac{1}{2} \int d^3 r' d^3 r \hat{\phi}_c(r) \hat{\phi}_c(r')} = \int \mathcal{D} \Phi_c e^{-\frac{1}{2} \int d^3 r' d^3 r \hat{\phi}_c(r) \hat{\phi}_c(r')},
\]
(8)
with the fluctuating potential $\hat{\phi}_c(r)$ associated with the Coulomb ($z = c$) or HC interactions ($z = h$). Then, passing from the canonical to the grand-canonical ensemble via the transformation
\[
Z_G = \sum_{N_w=1}^{\infty} \frac{A_{N_w}}{N_w!} \prod_{j=1}^{N_l} \sum_{N_j=1}^{\infty} \frac{A_{N_j}^j}{N_j!} Z_c,
\]
(9)
the grand-canonical partition function takes the functional integral form
\[
Z_G = \int \mathcal{D} \Phi e^{-\beta H_\Omega[F]},
\]
(10)
where we introduced the shortcut vector notations $\Phi = (\phi_c, \phi_h)$ and $\mathcal{D} \Phi = \mathcal{D} \phi_c \mathcal{D} \phi_h$.

In eqn (10), the electrolyte Hamiltonian
\[
H_\Omega[\Phi] = H_c[\Phi] + H_h[\Phi]
\]
(11)
is composed of the quadratic potential fluctuations and the contribution from the solvent molecules,
\[
\beta H_c[\Phi] = \frac{1}{2} \sum_{\alpha, \beta} \int d^3 r d^3 r' \phi_c(r) \phi_c(r') \phi_c(-r') - \int d^3 r d^3 r' \hat{\phi}_c(r) \hat{\phi}_c(r')
\]
(12)
and the component associated with the salt ions,
\[
\beta H_h[\Phi] = -\sum_{j=1}^{N_l} \int d^3 v \hat{\eta}_j(v).
\]
(13)
In eqn (12) and (13), we introduced the number density of the solvent and salt particles as
\[
\hat{\eta}_n(u, a) = A_w e^{-\omega_n(u, a)/\epsilon_n(u)} e^{-\epsilon_n(u - a/2)},
\]
(14)
\[
\hat{\eta}_j(v) = A_j e^{-\omega_j(v) + \epsilon_j(v) + \epsilon_j(v)}.
\]
(15)

B. Introducing the perturbative schemes
Due to the non-linear functional form of the solvent and salt densities in eqn (12) and (13), the partition function (10) cannot be evaluated analytically. In this section, we introduce a mixed perturbative treatment of the solvent and salt particles. This perturbative scheme will enable us the analytical evaluation of the salt-dressed solvent permittivity from the partition function (10).

1. Virial approximation for salt ions. In biological solutions, the typical salt concentrations located in the submolar range are by two orders of magnitude lower than the water concentration. This implies that the salt Hamiltonian (13) is the dilute component of the total Hamiltonian (11). Based on this point, we will treat the salt contribution (13) within a virial approximation. Thus, the remainder of the work will be limited to the linear order in the salt fugacity $O(A_j)$ or equivalently the salt concentration $O(p_j)$. The corresponding virial approximation will enable us to avoid the Gaussian-level treatment of the ion density that would limit the theory to the weak electrostatic coupling regime where the dielectric decrement by pure electrostatic ion–solvent interactions was observed to be absent.\(^{12,16,37}\)

In the grand-canonical ensemble, the statistical average of the general functional $F[\Phi]$ is defined as
\[
\langle F[\Phi] \rangle = \frac{1}{Z_G} \int \mathcal{D} \Phi e^{-\beta H_\Omega[F]} F[\Phi].
\]
(16)
Following the dilute salt approximation, we Taylor-expand eqn (10) and (16) at the linear order in the salt...
Hamiltonian (13). Upon this virial expansion, the field average (16) becomes

\[
\langle F(\Phi) \rangle \approx \langle F(\Phi) \rangle_w - \left\{ \langle \beta H_0(\Phi) F(\Phi) \rangle_w - \langle \beta H_0(\Phi) \rangle_w \langle F(\Phi) \rangle_w \right\},
\]

where we defined the statistical average over the solvent degrees of freedom governed by the Hamiltonian (12),

\[
\langle F(\Phi) \rangle_w = \frac{1}{Z_w} \int D\Phi e^{-\beta H_0(\Phi)} F(\Phi),
\]

with the solvent partition function \( Z_w = \int D\Phi e^{-\beta H_0(\Phi)} \).

2. Gaussian approximation for solvent particles. The non-linear dependence of the solvent Hamiltonian (12) on the fluctuating potentials \( \phi_c(\mathbf{r}) \) and \( \phi_h(\mathbf{r}) \) does not allow the analytical evaluation of the field-theoretic averages in eqn (18) over the solvent fluctuations. To progress further, we will approximate the solvent Hamiltonian by the following functional of quadratic dependence on the potentials \( \phi_c(\mathbf{r}) \) and \( \phi_h(\mathbf{r}) \),

\[
H_w \approx \frac{d^3 r_1 d^3 r_2}{2} \left\{ (\phi_c - i \phi_h) v_c^{-1}(\mathbf{r} - \mathbf{r}') (\phi_c - i \phi_h) v_c^{-1}(\mathbf{r} - \mathbf{r}')(\phi_h + \phi_h)(\mathbf{r} - \mathbf{r}') \right\}
\]

In eqn (19), we neglected the direct coupling between the fluctuating HC and electrostatic potentials, as well as the renormalization of the bare HC interaction potential \( v_0(\mathbf{r}) \) by many-body particle collisions. Moreover, we introduced the electrostatic potential \( \phi_h(\mathbf{r}) \) and the solvent kernel \( v_0(\mathbf{r} - r') \) that will be self-consistently determined from the solution of the SD equations.

Due to the quadratic form of the functional Hamiltonian (19), the calculation of the statistical average in eqn (17) reduces to the evaluation of Gaussian functional integrals. To this aim, we will extensively use the identity

\[
\langle e^{\int d\mathbf{r}[J_c(\mathbf{r}) \phi_c(\mathbf{r}) + J_h(\mathbf{r}) \phi_h(\mathbf{r})]} \rangle_w = e^{-\int d\mathbf{r}[J_c(\mathbf{r}) \phi_c(\mathbf{r}) + J_h(\mathbf{r}) \phi_h(\mathbf{r})]} \prod_{z=0,1,2} e^{\frac{1}{2} \int d\mathbf{r} J_z(\mathbf{r}) \phi_z(\mathbf{r}) \phi_z(\mathbf{r})}
\]

including the generating functions \( J_{c,h}(\mathbf{r}) \).

The remainder of the present work will be based on the solution of the electrostatic SD equations

\[
\left\langle \delta(\beta H_0(\Phi)) \right\rangle = 0,
\]

\[
\left\langle \delta(\beta H_0(\Phi)) \phi_c(\mathbf{r}) \right\rangle = \delta(\mathbf{r} - \mathbf{r}'),
\]

where the field averages will be calculated within the approximation schemes introduced above. Eqn (21) is a beyond-mean-field (BMF) Poisson identity, and eqn (22) corresponds to a kernel equation characterizing the electrostatic fluctuations in the liquid. The derivation of these formally exact identities is reported in Appendix A.

C. Calculation of the particle densities and the electroneutrality condition

In this part, we calculate first the average density of the ions and the solvent molecules, and relate their fugacity to their bulk concentration. Then, by evaluating the SD eqn (21), we show that the mixed perturbation scheme introduced in ref. 2.2 consistently satisfies the global electroneutrality condition. With the aim to simplify the notation, from now on, the argument of the Hamiltonian functionals will be omitted.

1. Relating the particle fugacities and concentrations. The average density of the salt ions follows from the partition function (10) via the identity \( \rho_j = -Z_G^{-1} \delta Z_c/\delta w_j(\mathbf{r}) = \langle \delta \rho(\mathbf{r}) \rangle \). Substituting eqn (13) into eqn (17), using the identity (20), and setting the onsite potential \( w_0(\mathbf{r}) \) to zero, the ion density follows at the order \( O(\lambda_j) \) as \( \rho_j = \lambda_j e^{-\phi_0(\mathbf{r})} \). Moreover, noting that the uniformity of the bulk ion concentration implies a uniform potential \( \phi_h(\mathbf{r}) = \phi_h \), the relation between the ion concentration and fugacity follows as

\[
\lambda_j = \rho_j e^{\phi_0[2(\rho_0(\mathbf{r}) - \rho(\mathbf{r}))]}.
\]

In order to calculate the average solvent density, we set \( w_0(\mathbf{r}, \mathbf{a}) = w_0(\mathbf{r}) \) and use the identity \( \rho_w = -Z_G^{-1} \delta Z_c/\delta w_w(\mathbf{r}) \) to get

\[
\rho_w = \int \frac{d^3 \mathbf{u}}{4\pi} \langle \delta \rho(\mathbf{u}, \mathbf{a}) \rangle.
\]

Plugging the function (14) into eqn (17), and evaluating the field-theoretic averages with the identity (20), after lengthy algebra, eqn (24) yields at the order \( O(\rho_j) \)

\[
\lambda_w = \rho_w e^{\phi_0[2(\rho_0(\mathbf{r}) - \rho(\mathbf{r}))]} (1 - \delta \rho).
\]

In eqn (25), the second virial coefficient originating from the salt-solvent interactions reads

\[
\delta \rho = \sum_{j=1}^{p} \rho_j \int d^3 h_i(\mathbf{k}, \mathbf{a}),
\]

where we introduced the Mayer function

\[
h_i(\mathbf{k}, \mathbf{a}) = e^{-v_0(\mathbf{k}) - q_j(v_0(k - a) - v_0(k + a))} - 1,
\]

and the C.M. distance \( \mathbf{k} = \mathbf{v} - \mathbf{u} \) between the salt ions and the solvent molecules. Finally, in order to evaluate the density of the terminal charges of the solvent molecules, we redefine the dipolar onsite potential as \( w_{\mathrm{wz}}(\mathbf{u}, \mathbf{a}) = w_{\mathrm{w}}(\mathbf{u} + \mathbf{a}/2) + w_{\mathrm{w}}(\mathbf{u} - \mathbf{a}/2) \). Using the identities \( \rho_{wz} = -Z_G^{-1} \delta Z_c/\delta w_{\mathrm{wz}}(\mathbf{r}) \), after some algebra, one obtains the expected result

\[
\rho_{wz} = \rho_w.
\]

2. Electroneutrality condition from the Poisson eqn (21).

In this part, we show that the global electroneutrality condition consistently follows from the beyond-MF Poisson eqn (21).
First, by combining eqn (17) and (21), the Poisson equation becomes at the order \( O(\rho) \)
\[
\left\langle \frac{\delta(\beta H_w)}{\delta \phi_s(\mathbf{r})} \right\rangle_w + \left\langle \frac{\delta(\beta H_s)}{\delta \phi_s(\mathbf{r})} \right\rangle_w - \left\langle \beta H_s \frac{\delta(\beta H_w)}{\delta \phi_s(\mathbf{r})} \right\rangle_w + \left\langle \beta H_s \frac{\delta(\beta H_s)}{\delta \phi_s(\mathbf{r})} \right\rangle_w = 0. \tag{29}
\]
Next, we substitute into eqn (29) the Hamiltonian components (12) and (13), and make use of the identity (20) to evaluate the functional averages over the solvent fluctuations. Using as well eqn (23), (25), and (28), after long algebra, eqn (29) becomes
\[
\int d^3r c^{-1}(\mathbf{r} - \mathbf{r}') \left[ \phi_0(\mathbf{r}') + \phi_s(\mathbf{r}') \right] - \sum_{j=1}^{p} \rho_j \rho_j = 0, \tag{30}
\]
where we defined the average potential component induced by the salt ions,
\[
\phi_s(\mathbf{r}) = \sum_{j=1}^{p} \rho_j \rho_j d^3v_0(\mathbf{r} - \mathbf{v}). \tag{31}
\]
Injecting into eqn (30) and (31) the Fourier transform of the Green’s functions
\[
v_s(\mathbf{r} - \mathbf{r}') = \int \frac{d^3q}{(2\pi)^3} e^{i\mathbf{r} \cdot \mathbf{q}} v_s(q) \tag{32}
\]
for \( z = \{0, c\} \), with the Fourier-transformed bulk Coulomb potential \( \tilde{v}_z(q) = q^2/(4\pi \varepsilon_0 q) \) in vacuum, and accounting for the uniformity of the average potentials, i.e. \( \phi_0(\mathbf{r}) = \phi_0 \) and \( \phi_s(\mathbf{r}) = \phi_s \), eqn (30) finally reduces to the electroneutrality condition for the salt ions, i.e.
\[
\sum_{j=1}^{p} \rho_j q_j^2 = 0. \tag{33}
\]

D. Calculation of the salt-dressed solvent permittivity from the electrostatic kernel

Here, we calculate the electrostatic Green’s function and obtain the dielectric permittivity of the solvent.

1. Derivation of the electrostatic kernel equation. The electrostatic Green’s function is defined as the variance of the electrostatic potential fluctuations,
\[
G(\mathbf{r} - \mathbf{r}') = \langle \phi(\mathbf{r}) \phi(\mathbf{r}') \rangle - \langle \phi(\mathbf{r}) \rangle \langle \phi(\mathbf{r}') \rangle. \tag{34}
\]
Using the identity (17) for the virial-expanded field average, at the order \( O(\rho) \), eqn (34) takes the form
\[
G(\mathbf{r} - \mathbf{r}') = \langle \phi(\mathbf{r}) \phi(\mathbf{r}') \rangle_w - \langle \phi(\mathbf{r}) \rangle_w \langle \phi(\mathbf{r}') \rangle_w + \langle \phi(\mathbf{r}) \rangle_w \langle \phi(\mathbf{r}') \rangle_w \langle \beta H_s \rangle_w + \langle \phi(\mathbf{r}) \rangle_w \langle \beta H_s \rangle_w \langle \phi(\mathbf{r}') \rangle_w + \langle \phi(\mathbf{r}) \rangle_w \langle \phi(\mathbf{r}') \rangle_w \langle \beta H_s \rangle_w \langle \phi(\mathbf{r}') \rangle_w. \tag{35}
\]
Substituting now the salt Hamiltonian (13) into eqn (35), and evaluating with eqn (20) the averages over the solvent configurations, the net Green’s function becomes
\[
G(\mathbf{r} - \mathbf{r}') = v_0(\mathbf{r} - \mathbf{r}') - \sum_{j=1}^{p} \rho_j q_j^2 \int d^3v_0(\mathbf{v} - \mathbf{r}') v_0(\mathbf{v} - \mathbf{r}'). \tag{36}
\]
Finally, by Fourier-transforming eqn (36) according to eqn (32), the inverse kernel follows at the order \( O(\rho) \) as
\[
\tilde{G}^{-1}(q) = \tilde{v}_0^{-1}(q) + \sum_{j=1}^{p} \rho_j q_j^2. \tag{37}
\]

The first term on the r.h.s. of eqn (37) embodies the dielectric screening induced solely by the solvent molecules, and its modification by the salt–solvent scattering. Then, the second term accounts for the direct Debye screening by the salt charges. In order to characterize the effect of salt on the solvent permittivity, we calculate now the kernel eqn (22) satisfied by \( v_0(\mathbf{r} - \mathbf{r}') \).

Plugging eqn (11) into the l.h.s. of eqn (22), and using eqn (17), at the order \( O(\rho) \), the kernel equation becomes
\[
\left\langle \frac{\delta(\beta H_w)}{\delta \phi_s(\mathbf{r})} \phi_c(\mathbf{r}') \right\rangle_w + \left\langle \frac{\delta(\beta H_s)}{\delta \phi_s(\mathbf{r})} \phi_c(\mathbf{r}') \right\rangle_w - \left\langle \beta H_s \frac{\delta(\beta H_w)}{\delta \phi_s(\mathbf{r})} \phi_c(\mathbf{r}') \right\rangle_w - \left\langle \beta H_s \frac{\delta(\beta H_s)}{\delta \phi_s(\mathbf{r})} \phi_c(\mathbf{r}') \right\rangle_w = \delta(\mathbf{r} - \mathbf{r}'). \tag{38}
\]
Next, we plug into eqn (38) the Hamiltonian components (12) and (13), and evaluate the functional averages over the solvent degrees of freedom with the identity (20). After long but straightforward algebra, the Green equation satisfied by the solvent kernel \( v_0(\mathbf{r} - \mathbf{r}') \) finally follows as
\[
\int d^3r_1 c^{-1}(\mathbf{r} - \mathbf{r}_1) v_0(\mathbf{r}_1 - \mathbf{r}') + \sum_{j=1}^{p} \rho_j q_j^2 v_0(\mathbf{r} - \mathbf{r}')
+ Q^2 \rho_s \int \frac{d^3\Omega}{4\pi} \int d^3v \int d^3v' \int d^3v'' d^3v'''
\times \left[ h_1(\mathbf{v} - \mathbf{v}' + \frac{\mathbf{a}}{2}) - h_1(\mathbf{v} - \mathbf{v}' - \frac{\mathbf{a}}{2}) \right] v_0(\mathbf{v}') v_0(\mathbf{v} - \mathbf{v}')
- \sum_{j=1}^{p} \rho_j q_j^2 \int d^3v d^3r_1 c^{-1}(\mathbf{r} - \mathbf{r}_1) v_0(\mathbf{r}_1 - \mathbf{v}) v_0(\mathbf{v} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \tag{39}
\]
For the sake of consistency with the perturbative treatment of salt, eqn (39) should be linearized in the salt concentration. To this aim, we formally express the solution to eqn (39) as
\[
v_0(\mathbf{r} - \mathbf{r}') = v_w(\mathbf{r} - \mathbf{r}') + \lambda v_s(\mathbf{r} - \mathbf{r}'), \tag{40}
\]
where the kernel component \( v_w(\mathbf{r} - \mathbf{r}') \) is associated with pure solvent, and the correction term \( v_s(\mathbf{r} - \mathbf{r}') \) accounts for the solvent–salt correlations. In eqn (40), we introduced the dimensionless perturbative parameter \( \lambda = O(\rho) \) that will be set to unity.
at the end of the calculation. Plugging eqn (40) into eqn (39), and expanding the result at the order $O(\rho_j)$, one obtains the following integral equations satisfied by each kernel component,

$$
\int d^3r v_\omega^{-1}(r-r_1)v_\omega(r_1-r') + Q^2 \rho_w
\times \int \frac{d^3\Omega}{4\pi} [2v_\omega(r-r') - v_\omega(r-a-r') - v_\omega(r+a-r')] = \delta(r-r'),
$$

(41)

and the following integral equations satisfied by each kernel with the expanded Mayer function

$$
\int d^3r v_\omega^{-1}(r-r_1)v_\omega(r_1-r')
+ Q^2 \rho_w \int \frac{d^3\Omega}{4\pi} [2v_\omega(r-r') - v_\omega(r-a-r') - v_\omega(r+a-r')]
+ Q \rho_w \sum_{j=1}^p \rho_j q_j \int d^3r v_\omega(r-r')
\times v_\omega(v-r') + \sum_{j=1}^p \rho_j q_j^2 v_\omega (r-r')
- \sum_{j=1}^p \rho_j q_j^2 \int d^3v d^3r v_\omega^{-1}(r-r_1)v_\omega(r_1-v)v_\omega(v-r') = 0,
$$

(42)

with the expanded Mayer function

$$
h_j(k, a) = e^{-\kappa_0(k-a)} + \kappa_0^2 \left[ 1 - \frac{\sin(qa)}{qa} \right].
$$

(43)

2. Solution of the kernel eqn (41) and (42). Eqn (41) is an integro-differential equation satisfied by the salt-free solvent kernel.12 By Fourier-transforming this identity according to eqn (32), and evaluating the integral over the solid angle $\Omega$, the solution directly follows as the non-local Coulomb law firstly derived in ref. 12,

$$
\tilde{v}_\omega^{-1}(q) = \frac{q^2 \tilde{\varepsilon}_\omega(q)}{4\pi \ell_B}; \quad \tilde{v}_\omega(q) = 1 + \frac{\kappa_w^2}{q^2} \left[ 1 - \frac{\sin(qa)}{qa} \right].
$$

In eqn (44), we introduced the dielectric permittivity spectrum $\tilde{\varepsilon}_\omega(q)$ with the dielectric screening parameter

$$
\kappa_w = \sqrt{8\pi Q^2 \ell_B \rho_w}.
$$

(45)

In the infrared (IR) limit, this permittivity function tends to the static dielectric permittivity of the pure solvent, i.e. $\varepsilon_w(q \to 0) = \varepsilon_w, b$, with the bulk solvent permittivity given by the Debye-Langevin equation

$$
\varepsilon_w, b = 1 + 4\pi \frac{\lambda}{3} Q^2 a^3 \rho_w.
$$

(46)

Eqn (46) quantifying the dielectric response of a weakly interacting dipolar fluid is a consequence of the WC Gaussian approximation introduced in Section 2.2.2 to treat the solvent–solvent interactions. In Conclusions, we discuss a potential approach enabling the relaxation of this WC approximation. We also note that unless stated otherwise, in the remainder, we will set the dipole length to the value $a = 1 \text{ Å}$ yielding the water permittivity $\varepsilon_w, b \approx 78.8$ at the temperature $T = 298 \text{ K}$.

In order to derive the correction kernel $v_s(r-r')$, we plug into eqn (42) the Fourier expansion of the Green’s functions in eqn (32). Carrying out the spatial and angular integrals, after some algebra, the Fourier-transformed correction kernel follows as

$$
\tilde{v}_s(q) = -\sum_{j=1}^p \rho_j q_j \{ q_j [1 - \varepsilon_w^{-1}(q)] + Q \rho_w T_j(q) \} \tilde{v}_w^2(q),
$$

with the auxiliary integral

$$
T_j(q) = \int \frac{d^3\Omega}{4\pi} k^i k^j [h_j \left( \frac{k+a}{2} \right) - h_j \left( \frac{k-a}{2} \right)] e^{q_k k}.
$$

(47)

Hence, the Fourier-transformed inverse of eqn (40) given by $\tilde{\nu}_0^{-1}(q) = \tilde{\varepsilon}_w^{-1}(q) - \tilde{v}_w^{-2}(q) \tilde{v}_w(q) + O(\rho_j^2)$ becomes

$$
\tilde{\nu}_0^{-1}(q) = \frac{q^2 \tilde{\varepsilon}_w(q)}{4\pi \ell_B}
+ \sum_{j=1}^p \rho_j q_j \{ q_j [1 - \varepsilon_w^{-1}(q)] + Q \rho_w T_j(q) \}.
$$

(48)

3. Computation of the salt-dressed dielectric permittivity. Injecting now eqn (48) into eqn (37), the inverse total kernel follows as

$$
\tilde{G}^{-1}(q) = \frac{1}{4\pi \ell_B} \sum_{j=1}^p \left[ \kappa_j^2 + \delta \kappa_j^2 \right] + \frac{q^2 \tilde{\varepsilon}(q)}{4\pi \ell_B},
$$

(49)

with the Fourier transform of the electrolyte permittivity

$$
\tilde{\varepsilon}(q) = \tilde{\varepsilon}_w(q) + \delta \tilde{\varepsilon}(q).
$$

(50)

In eqn (49), we introduced the DH parameter associated with each ion species as $\kappa_j^2 = 4\pi \varepsilon_w \rho_j a^3$, with the Bjerrum length in water $\ell_w = \ell_w^b / \varepsilon_w^b$. Moreover, we defined the following correction terms embodying the effect of the solvent-salt correlations on the Debye screening and the dielectric permittivity,

$$
\delta \kappa_j^2 = \kappa_j^2 \left[ \frac{Q \rho_w T_j(0) + \varepsilon_w - 1}{\varepsilon_w, b} \right],
$$

(51)

$$
\delta \tilde{\varepsilon}(q) = \sum_{j=1}^p \frac{\kappa_j^2}{q^2} \left[ \frac{\varepsilon_w, b \rho_w [T_j(q) - T_j(0)]}{q_j} + 1 - \frac{\varepsilon_w - 1}{\varepsilon_w, b} \right].
$$

(52)

For the evaluation of eqn (51) and (52), we reduce the integral (47) to a numerically manageable form. Substituting the Mayer function (43) into eqn (47), the latter becomes

$$
T_j(q) = \int \frac{d^3k}{4\pi} k^i k^j K_j(k, q),
$$

(53)

where we introduced the auxiliary integral

$$
K_j(q, k) = \int \frac{d^3\Omega}{4\pi} \left\{ e^{-q_j k a^2} - q_j \rho_w \varepsilon_w, b \left[ e^{-q_j k a^2} - \varepsilon_w - 1 \right] \\
- e^{-q_j k a^2} + q_j \rho_w \varepsilon_w, b \left[ e^{-q_j k a^2} - \varepsilon_w - 1 \right] \right\}.
$$

(54)
Noting that the HC and Coulomb potentials in eqn (54) depend exclusively on the magnitude of their argument, this integral can be expressed as

$$K_j(q, k) = \frac{\int d^3 \Omega}{4\pi} \left\{ e^{-\frac{\theta}{k} |u|} - e^{-\frac{\theta}{k} |q|} \right\} \cdot \left\{ e^{-\frac{\theta}{k} |v|} - e^{-\frac{\theta}{k} |w|} \right\},$$

(55)

where we defined the variables $u = \sqrt{k^2 + a^2/4 + k \cdot a}$ and $t = \sqrt{k^2 + a^2 + 2k \cdot a}$. Considering now the specific HC interaction potential defined by eqn (1), and expressing the integral (55) in terms of the spherical coordinates associated with a Cartesian coordinate system whose z axis aligns with the vector $k$, one obtains

$$K_j(q, k) = \frac{\int d^3 \ell}{4\pi} \sin \theta \left\{ e^{-\ell q} |u| - v |w| \right\} \cdot \left\{ e^{-\ell q} |v| - w |k| \right\},$$

(56)

where

$$u = \sqrt{k^2 + a^2/4 + k \cdot a}, \quad t = \sqrt{k^2 + a^2 + 2k \cdot a}.$$  

Finally, changing the integration variable in eqn (56) from $\theta$ to $\ell$, one obtains

$$T_j(q) = \frac{4\pi}{a} \int d|k| \sin \theta \left\{ e^{-\ell q} |u| - v |w| \right\} \cdot \left\{ e^{-\ell q} |v| - w |k| \right\},$$

(57)

with the cut-off distance accounting for the HC interactions $t = (k - a, \sqrt{2d^2 - k^2 + a^2/2})$.

The static permittivity of the electrolyte corresponds to the IR limit of the Fourier-transformed permittivity function (50), i.e. $\varepsilon_b = \varepsilon(q \to 0) = \varepsilon_{wb} + \delta\varepsilon(q \to 0)$. Substituting the integral (57) into eqn (51) and (52), and taking the IR limit, the correction to the screening parameter and the electrolyte permittivity finally follow as

$$\delta\varepsilon_j^2 = K_j^2 \left\{ \varepsilon_{wb} - \varepsilon_{wb}^{(1)} \right\},$$

(58)

$$\varepsilon_b = \varepsilon_{wb} - \frac{\pi \varepsilon_{wb}^2}{a} \int d|k| \cdot \left\{ e^{-\ell q} |u| - v |w| \right\} \cdot \left\{ e^{-\ell q} |v| - w |k| \right\},$$

(59)

where we introduced the auxiliary integrals

$$T_j^{(a)} = \frac{4\pi}{a} \int d|k| \sin \theta \left\{ e^{-\ell q} |u| - v |w| \right\} \cdot \left\{ e^{-\ell q} |v| - w |k| \right\},$$

(60)

embodying the HC and electrostatic interactions between the salt charges and the solvent molecules.

At this point, we note that the numerical computation of the integrals in eqn (60) requires the knowledge of the non-local electrostatic potential $v_0(r)$ in the pure solvent. This potential follows from eqn (32) and (44) as

$$v_0(r) = \frac{\varepsilon_b}{\varepsilon_b(r)r}, \quad \varepsilon_b(r) = \frac{\varepsilon_b}{2} \left\{ \int dq \sin(qr) \right\}^{-1},$$

(61)

where $\varepsilon_b(r)$ is the non-uniform permittivity characterizing the dielectric screening induced by the structured solvent at a distance $r$ from a charge source. As this distance increases, the non-uniform permittivity tends to the bulk value given by the Debye–Langevin eqn (46), i.e. $\varepsilon_b(r \to \infty) = \varepsilon_{wb}$ (see Fig. 4(c) below).

From the numerical evaluation of the integral $T_j^{(a)}$ in the second term of eqn (58), we found that for salts of arbitrary composition, the correction to the Debye screening in eqn (49) is exactly zero, i.e.

$$\sum_{j=1}^{p} \delta\varepsilon_j^2 = 0.$$  

(62)

Thus, at the leading order, the ion–solvent correlations modify exclusively the solvent-induced dielectric screening without affecting the salt-driven Debye screening.

We finally calculate the modification of the solvent permittivity profile in eqn (61) by added salt. From eqn (37) and (49), the inverse Fourier-transformed electrostatic interaction potential excluding the Debye screening follows as $\varepsilon_0^{-1}(q) = q^2 \varepsilon(q)/(4\pi \varepsilon_0)$. Passing from the reciprocal to the real space via an inverse Fourier transform, and expanding the result at the linear order in the salt concentration, the non-local electrostatic potential and the salt-dressed permittivity profile become

$$v_0(r) = \frac{\varepsilon_0}{\varepsilon_0(r)r}; \quad \varepsilon_b(r) = \varepsilon_w(r) + \delta\varepsilon(r) + O(\rho_j^2),$$

(63)

where the permittivity correction associated with the salt–solvent correlations reads

$$\delta\varepsilon(r) = \frac{2\varepsilon_0(r)}{\pi} \int_0^{\infty} d|q| \sin(qr) \delta\varepsilon(q).$$

(64)

III. Results and discussion

A. Salt-induced dielectric decrement

The permittivity formula in eqn (58) is the key result of this article. One notes that this identity displays explicitly the experimentally observed linear decrement of the liquid permittivity with the dilute salt concentration $\rho_j$. Fig. 2(a) illustrates the theoretical prediction (58) (dashed curve) and the experimental permittivity data of various monovalent salt solutions against the salt concentration $\rho_\pm = \rho_s$ at the liquid temperature $T = 298$ K. The HC diameter is set to the value $d = 1.485$ Å yielding the best agreement with the slope of the NaCl permittivity data. The plot shows that the linear decrement of the permittivity occurs in the density regime $\rho_s \lesssim 2.0$ M.

In order to shed light on the nature of the particle correlations driving the dielectric decrement, we note that the integrals (53)–(54), or equivalently the integral (59) in eqn (58) correspond to the trace of the Mayer functions (43) associated with the interacting salt ($q_j$) and solvent charges ($\pm$) over the ion and dipole configurations. Thus, according to eqn (58), the dielectric decrement is the manifestation of the salt-induced electrostatic screening of the polarization charges reducing the dielectric response of the solvent. Next, we investigate the role
of the liquid temperature, the HC and solvent radii, and the ion valency on this decrement mechanism.

B. Effect of temperature

The temperature dependence of the liquid permittivity is illustrated in Fig. 2(b). One notes that at various salt concentrations, the permittivity formula (58) can qualitatively reproduce the decay of the experimental NaCl permittivity with the rise of the temperature, i.e. $T \uparrow \varepsilon_b \downarrow$. This feature is equally illustrated in Fig. 3(a–d) displaying the dielectric decrement by salt at various temperatures. One sees that at submolar salt concentrations, eqn (58) can account for the permittivity decrease by the rise of the temperature with reasonable accuracy. Beyond the submolar concentration regime, the breaking of the virial approximation at the basis of our formalism leads to the overestimation of the experimental permittivity data at all temperatures.

In Fig. 2(b), the qualitatively identical decline of the water (blue) and electrolyte permittivities (black and red) indicates that the thermal decay is mainly caused by the suppression of the dielectric response of the background solvent by the amplification of the thermal fluctuations. One also notes that the slope or equivalently the thermal susceptibility of the experimental data is underestimated by eqn (58). In the submolar concentration regime of Fig. 3(a–d), this translates into the underestimation of the experimental data by eqn (58) at low temperatures and its overestimation at high temperatures.

In Fig. 2(b), the similar deviation of the theoretical result from the experimental data for pure water and electrolytes suggests that the underestimation of the thermal susceptibility of the permittivity by our formalism may originate from the WC treatment of the dipole–dipole correlations leading to the Debye–Langevin relation (46) for pure solvent. In order to verify this point, we characterize next the thermal susceptibility of the salt-induced dielectric decrement by isolating the latter from the temperature dependence of the background water.

In Fig. 3(e–h), we reported the permittivity decrement $\Delta \varepsilon_b = \varepsilon_b - \varepsilon_{w,b}$ against the salt concentration at various temperatures. First, from the top to the bottom plot, the inspection of the experimental data and the theoretical curves with respect to the right axis shows that the rise of the temperature lowers the magnitude of the dielectric decrement, i.e. $T \uparrow |\Delta \varepsilon_b| \downarrow$. According to eqn (58), this feature stems from the weakening of the salt–solvent correlations by thermal fluctuations. Namely, in eqn (59), the rise of the temperature reduces the magnitude of the dimensionless electrostatic potential $v_w(r)$ mediating the electrostatic salt–solvent interactions. This weakens the salt screening of the polarization charges and suppresses the resulting dielectric decrement.

In Fig. 3, one also notes that the thermal decay of the dielectric decrement $\Delta \varepsilon_b$ excluding the dielectric response of the pure solvent is reproduced by eqn (58) with a significantly better accuracy than the decay of the total permittivity $\varepsilon_b$. This suggests that the underestimation of the thermal susceptibility...
of the liquid permittivity by our approach originates mainly from the WC-level one-loop treatment of the background solvent. It should be however noted that the hydrogen bond formation in the solvent may also play a role in the quantitative deviation of the theoretical curves from the experimental data. Potential improvements of our solvent model and the treatment of the underlying many-body dipole–dipole interactions are elaborated in Conclusions.

C. Effect of HC and solvent radii, and salt valency

Fig. 2(c) illustrates the influence of the HC radius, the solvent size, and the salt valency on the dielectric decrement. The plot is limited to the physical regime of positive dielectric permittivity below which the virial treatment of the salt ions at the basis of our formalism breaks down. The figure shows that the electrolyte permittivity exhibits a high sensitivity to the solvent and HC radii.

First, one sees that at constant ratio $d/a$, the lower the solvent size, the stronger the dielectric decrement, i.e. $a \downarrow \varepsilon_{w,b} \downarrow$. To understand this point, we note that according to eqn (46), the reduction of the solvent size $a$ or equivalently the dipole moment $\mu = qa$ lowers the solvent permittivity $\varepsilon_{w,b}$. This weakens the dielectric screening experienced by the interaction potential $\varepsilon_{w,r}(r)$ in eqn (59), amplifying the magnitude of the salt–solvent correlations and the resulting dielectric decrement.

In Fig. 2(c), the comparison of the solid and dotted blue curves shows that salt valency plays a similar role on dielectric decrement. Namely, in eqn (59), a higher salt valency gives rise to stronger salt–solvent correlations. As a result, the addition of a $1:2$ salt into water leads to a more efficient dielectric decrement than a monovalent $1:1$ salt, i.e. $q_j^1 \downarrow \varepsilon_{w,b} \downarrow$. It is noteworthy that this effect has been observed in the experiments of Harris and O’Konski conducted with mono- and divalent salt solutions.\textsuperscript{25}

Finally, Fig. 2(c) shows that the electrolyte permittivity is a uniformly rising function of the HC size, i.e. $d \uparrow \varepsilon_{w,b} \uparrow$. This feature stems from the overall attenuation of the salt–solvent correlations by the increase of the close contact distance. This suppresses the dielectric decrement and rises the permittivity of the $1:1$ solutions towards the water permittivity $\varepsilon_{w,b}$ reached at the contact distance $d \approx 1.5a$. In the case of the $1:2$ solutions characterized by stronger salt–solvent coupling (dotted curve), the dielectric decrement exhibits a sharper decay with the rise of the HC diameter, and the water permittivity is reached at the larger HC size of $d \approx 2a$.

D. Spatial structure of the dielectric decrement

We have so far analyzed the salt-induced decrement of the bulk permittivity (58) characterizing the dielectric screening ability of the electrolyte at large distances from charge sources. Here, we scrutinize the spatial structure of the dielectric decrement in the close vicinity of charges.

1. Modification of the dielectric spectrum by added salt.
The electrolyte permittivity can be experimentally measured at different wavelengths.\textsuperscript{14,23–25} Motivated by this point, we characterize first the spatial spectrum of the salt-dressed permittivity. To this aim, in Fig. 4(a and b), we reported the Fourier-transformed electrolyte permittivity (50) and its salt component (64) at various solute concentrations. One sees that as the wavelength $q$ rises, the pure solvent permittivity (black) uniformly drops from the bulk permittivity $\varepsilon_{w,b}$ to the vacuum permittivity $\varepsilon_v(q \rightarrow \infty) = 1$ corresponding to the dielectric void in the vicinity of charge sources.\textsuperscript{15,12} However, upon salt addition, the dielectric spectrum acquires a non-uniform dependence on the wavelength.

To understand the change of the dielectric spectrum, we note that in Fig. 4(b), salt addition into the solvent gives rise to a substantial dielectric decrement $(\delta\varepsilon(q) < 0)$ at short wavelengths $qa \leq 2$ and a weak dielectric increment $(\delta\varepsilon(q) > 0)$ in the regime $qa \geq 2$ of long wavelengths. As a result, Fig. 4(a) shows that added salt lowers the dielectric permittivity in the short wavelength regime and moves the peak of the permittivity spectrum from the strict IR limit $q = 0$ to a finite wavelength value $q = q^*$ rising with the salt concentration $(\rho_s \uparrow q^* \uparrow)$. Below, we investigate the impact of this peculiarity on the range of the non-local dielectric screening in real space.
2. Effect of added salt on the spatial permittivity profile. Fig. 4(c and d) display the permittivity profile in eqn (62) and the salt-driven decrement function (63) at various solute concentrations. In the case of a pure solvent (solid black curve), the permittivity is characterized by a region of dielectric deficiency \((\varepsilon(r) < \varepsilon_{w,b})\) followed by a high dielectric increment peak \((\varepsilon(r) \gg \varepsilon_{w,b})\) and an oscillatory convergence towards the bulk permittivity \(\varepsilon_{w,b}\) (dotted curve). In ref. 11 and 12, we showed that the corresponding dielectric structure equally observed in AFM experiments\(^4\) and MD simulations\(^5,6\) originates from the particularly strong self-screening of the polarization charges at the large solvent concentration.

In Fig. 4(c and d), one sees that salt addition into the solvent leads to the spatially non-uniform decrement of the liquid permittivity; one notes that salt–solvent correlations lead to the maximum amount of dielectric decrement around the first permittivity peak where the dielectric response of the solvent is the strongest, while the liquid region around \(r \approx a\) characterized by the weakest dielectric response experiences an insignificant dielectric decrement. One also sees that added salt approaches the location of the dielectric peak from \(r \approx a/2\) towards the source charge located at \(r = 0\). This indicates that the addition of salt reduces not only the magnitude but also the range of the dielectric screening by solvent.

For a systematic characterization of the correlation between the strength of the solvent–solute interactions and the liquid permittivity profile, in Fig. 4(e and f), we plotted the dielectric permittivity and the decrement functions at various HC diameters. The plots show that as the HC diameter is lowered from \(d = 1.5a\) to \(a\), the intensification of the salt–solvent correlations flattens the permittivity profile by suppressing the minima and maxima beyond the first dielectric peak. Hence, in addition to lowering the range and the magnitude of the liquid permittivity, salt–solute correlations also attenuate the dielectric structure in the vicinity of charge sources and suppress the non-locality of the electrostatic interactions.

IV. Conclusions

Within a field-theoretic explicit solvent formalism, we characterized the electrostatic mechanism behind the salt-driven dielectric decrement. By accounting for the finite size of the solvent molecules, we avoided the UV divergence issue bypassed in point-dipole models with a UV cutoff. The key novelty of our formalism is the relaxation of the WC treatment of salt used by earlier models of dipolar liquids.\(^5,2,36,37\) More precisely, by exploiting the contrast between the concentration of the dense solvent and the substantially more dilute salt component of the electrolyte, we incorporated the salt fluctuations via a virial expansion. Upon this virial approximation that enabled the explicit inclusion of the many-body salt–solvent interactions, the experimentally observed linear dielectric decrement by dilute salt addition emerged directly in the form of the permittivity formula (58).

The analytical formula (58) allows to identify clearly the electrostatic mechanism behind the dielectric decrement as the salt screening of the polarization charges suppressing the dielectric response of the polar liquid. The comparison of the theoretical prediction (58) and the experimental permittivity data indicates that the virial approximation underlying our formalism holds up to the characteristic salt concentration \(\rho_s \sim 2 M\). It is noteworthy that the latter is much larger than the characteristic multivalent ion density \(\rho_s \sim 10^{-3} M\) marking the validity regime of the solvent-implicit dressed ion approaches employing a similar virial approximation.\(^39\) This contrast can be explained by the fact that the dominant component of solvent-implicit electrolyte mixtures is the monovalent salt of submolar concentration, while the major component of our explicit solvent model is the polar liquid of substantially larger density \(\rho_w = 55 M\).

By direct confrontation with experimental data, we showed that our theory can reproduce qualitatively the decrease of the electrolyte permittivity with the rise of the temperature, as well as the thermal decay of the dielectric decrement with reasonable quantitative accuracy. Considering that our formalism models salt ions as point-charges and therefore neglects the thermal variation of the electronic cloud radius determining the HC size, the overall agreement with experiments reached with a single adjusted value of the HC diameter is rather remarkable.

Via the incorporation of the ion polarizability or more general ionic structures into our formalism, the point charge approximation for the salt ions can be relaxed in upgraded models. This extension would allow to include the thermal variation of the HC size together with the ionic specificity into our model. It should be however noted that the incorporation of the ionic polarizability or an extended ion charge structure would equally require the inclusion of the incompressible water condition expected to affect the extension of the electronic cloud radius. These important generalizations of substantial complexity are beyond the scope of the present study and they should be considered in future works.

It was shown that that the attenuation of the dielectric decrement by the rise of the temperature originates from the suppression of the solvent-ion correlations by thermal fluctuations. We also found that due to the amplification of the same correlations with rising valency, added 2:1 salts induce a more efficient dielectric decrement than 1:1 salts. This prediction agrees qualitatively with the experiments of Harris and O’Konski carried out with symmetric and asymmetric electrolytes.\(^25\)

In Fig. 3, we also showed that eqn (58) predicts the thermal variation of the permittivity decrement \(\Delta \varepsilon_b\) more accurately than the net electrolyte permittivity \(\varepsilon_b\) dominated by the background solvent. This point indicates that the underestimation of the thermal susceptibility of the permittivity data by our formalism stems mainly from the Gaussian-level treatment of the pure solvent correlations leading to the Debye–Langevin identity (46). Via the calculation of the dielectric permittivity from the fluctuation–dissipation theorem, we are currently working on the relaxation of the WC treatment of solvent beyond the Debye–Langevin-level. This extended approach will be presented in an upcoming article.
We emphasize that the field-theoretic structure of our formalism enables a smooth extension of the underlying theory to inhomogeneous liquids. Namely, the reevaluation of the Poisson eqn (29) and the kernel eqn (38) without assuming the spherical symmetry of the present model would yield the first solvent-explicit theory of confined liquids explicitly accounting for the salt-induced dielectric decrement. From nanofluidic ion and molecular transport governed by the dielectric response of the confined liquid3,41,42,45–48 to electrostatic potential and linearize the result in terms of the function \( \delta \phi_c(r) \). The resulting variation of the integral (A1) follows as

\[
\delta I = \frac{dF[\Phi]}{d\phi_c(r)} \left[ D \Phi e^{-\beta H_\alpha[\Phi]} \right] \cdot \frac{\delta F[\Phi]}{\delta \phi_c(r)}
\]

At this point, we note that the potential shift \( \delta \phi_c(r) \) can be removed via the redefinition of the integration measure in eqn (A1), implying the invariance of the integral (A1) under the shift by \( \delta \phi_c(r) \), i.e. \( \delta I = 0 \). Thus, setting the r.h.s. of eqn (A2) to zero, and dividing the result by the partition function (10), one gets

\[
\left< \frac{\delta F[\Phi]}{\delta \phi_c(r)} \right> = \left< F[\Phi] \frac{\delta H_\alpha[\Phi]}{\delta \phi_c(r)} \right>.
\]

By setting in eqn (A3) \( F[\Phi] = 1 \) and \( F[\Phi] = \phi_c(r) \), one obtains respectively the formally exact SD equations

\[
\frac{\delta (\beta H_\alpha[\Phi])}{\delta \phi_c(r)} = 0,
\]

\[
\frac{\delta (\beta H_\alpha[\Phi])}{\delta \phi_c(r)} \phi_c(r) = \delta (r - r')
\]

corresponding to eqn (21) and (22) in the main text.

### References


13. We note that the functional form of the dielectric permittivity profile in eqn (34) of ref. 11 at charged membranes is identical to the dielectric permittivity function in eqn (32) of ref. 12 in bulk liquids. This indicates that in the vicinity of charge sources, bulk and confined solvents are characterized by a similar dielectric permittivity structure.


This numerically revealed feature that we have not been able to explain by a simple mathematical argument implies that the second term in the curly bracket of eqn (57) exactly cancels out the first term proportional to the susceptibility of the pure solvent.