

Nonlocal dielectric response of aqueous electrolytes and decay behavior of ionic correlations

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We present molecular dynamics simulation results for the static nonlocal dielectric function, $\epsilon(k)$, and ion-ion correlations in aqueous electrolytes across various concentrations, analyzed within the framework of statistical mechanical theory. We investigate the complicated behavior of $\epsilon(k)$ and its influence on the screening patterns of ionic electric fields. At large to moderate values of the wave number k , $\epsilon(k)$ is primarily governed by the molecular structure of water, even at concentrations up to 1 M. However, at higher concentrations, ionic structuring begins to diminish water's influence. In agreement with the theoretical analysis presented, both Debye-type plain exponential and exponentially decaying oscillatory contributions to the electrostatic interactions are obtained for low electrolyte concentrations of NaCl in water. The latter originate from the water structure, while the former can be quantitatively described up to at least 2 M solutions by using a Debye length calculated with a concentration-dependent “dielectric constant” obtained by simulations. The theoretical basis for the use of such a “constant” is examined. At higher concentrations, there are only oscillatory contributions to the interactions. In our simulations, we do not have long-range monotonic interactions of the type reported in surface force measurements at concentrations above 1 M NaCl in water, often referred to as “anomalous underscreening.” Instead, we find a Debye-type decay, modified by an electrolyte-concentration-dependent effective dielectric constant. This behavior is seen up to at least 2 M concentrations, with decay lengths significantly shorter than those associated with underscreening.

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I. INTRODUCTION

The theory of electrolytic solutions is a venerable branch of physical science, attracting sustained attention from physicists and chemists for over 150 years [1]. Its enduring relevance stems from the pivotal role of electrolytes in diverse fields, ranging from chemical kinetics and electrochemistry—including electrocatalysis and energy conversion/storage [2]—to mineral extraction [3], water desalination [4], and biological systems where electrolytic media dominate the intracellular environment [5]. Historically, theoretical progress was guided by continuum models treating the solvent as a uniform dielectric medium. With time, attention gradually shifted toward molecular-level descriptions, aligning the field more closely with the broader development of liquid-state physics.

For physicists, electrolyte solutions offered a fascinating analogy to classical ionic plasmas, albeit existing at room temperature. These systems have served as critical testbeds for statistical mechanical methods [6–8]. Early

theoretical efforts focused on the ionic subsystem, often neglecting the molecular granularity of the solvent. However, the advent of solvent-free ionic liquids—ultraconcentrated room-temperature plasmas—spurred renewed interest in concentrated electrolyte solutions [9] and water in salt electrolytes [10], where such an approach was to be abandoned. This resurgence has driven substantial advances through various experimental techniques (e.g., scattering [11,12] and force measurements [13–17]), modern statistical mechanical theory [18–23], and computer simulations [24–29].

A central theoretical challenge, which remains only partially resolved, concerns the coupling between solvent structure and interionic correlations [30]. One promising avenue of progress addresses this by considering spatial dispersion in the dielectric response, namely, the inherent nonlocality of electrostatic interactions in electrolytes [31]. In this framework, a particle's response depends not only on the local electrostatic field but also on the field in its surrounding region. This behavior is formally captured by the wavevector-dependent dielectric function $\epsilon(k)$, whose k dependence reflects the microscopic structure of the fluid and the many-body correlations of the electrolytes—an area that has recently gained renewed interest due to the advances in understanding field screening and correlations in dense ionic systems.

In electrolyte theory, neglecting this nonlocality reduces the theoretical treatment to the Poisson-Boltzmann (PB) approximation, wherein the potential of mean force w_i on an ion of species i located at $\mathbf{r} = (x, y, z)$ is given by

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$w_i(\mathbf{r}) = q_i\phi(\mathbf{r})$, with q_i the ionic charge and $\phi(\mathbf{r})$ the electrostatic potential. This approximation yields only a single decay mode governed by the Debye length. In reality, however, w_i for all species depends on $\phi(\mathbf{r}')$ for $\mathbf{r}' \neq \mathbf{r}$ because any particle located at $\mathbf{r}'$ contributes to $w_i(\mathbf{r})$ via interparticle correlations. The many-body correlations, which give this nonlocality, lead to a richer structure, giving rise to multiple decay modes with distinct decay lengths, some of which are oscillatory. Capturing these features is essential for a comprehensive understanding of electrolyte solutions.

Beyond the bulk phase, the fundamental decay modes also play a central role in determining interfacial and confinement effects. In particular, the long range distance behavior of surface forces between surfaces immersed in electrolytes is governed by the same fundamental decay modes as those of the bulk pair correlation functions, with the amplitudes modulated by the boundary conditions at the surfaces [30,32–34]. Experimental surface force measurements for ionic liquids and concentrated electrolyte solutions have revealed force profiles combining a very long-range monotonic contribution together with short-range oscillations; see Ref. [35] for a recent review. The existence of such long-ranged forces has been denoted as “anomalous underscreening” because the Debye-type decay mode predicted by the PB approximation has a short decay length under these conditions [36,37]. For the forces measured in aqueous NaCl solutions, such a long-ranged contribution starts to appear for concentrations above 1 M [14], whereby the decay length becomes much larger than the Debye length.

Complementary insights regarding interactions in aqueous electrolyte solutions have been obtained by all-atom molecular dynamics (MD) simulations with explicit solvent [28,29,38,39]. Recent simulation studies have further explored various aspects of ionic correlations and screening phenomena in these systems [40–42]. Notable discrepancies exist between simulation and experimental observations. For instance, in 4.43 M aqueous NaCl solution, Zeman *et al.* [29,38] reported that the decay of the ionic pair-correlation function consisted solely of oscillatory contributions, with no detectable monotonic component. The same is true in simulations of other systems at high electrolyte concentrations [28]. The decay length of the oscillatory contribution is about one or two molecular diameters, which is larger than the Debye length, but no monotonic part appears. These contrasting results highlight the complex interplay between correlation structure, dielectric response, and electrolyte concentration—underscoring the need for a deeper theoretical understanding of screening behavior in concentrated aqueous electrolytes.

To advance this understanding, we focus on analyzing the wavevector-dependent dielectric function $\varepsilon(k)$, which characterizes the *linear polarization response*. While $\varepsilon(k)$ inherently captures the nonlocal nature of screening, the full electrostatic response of the electrolyte is more complex, exhibiting nonlinear effects and excluded volume considerations that go beyond linear response [43–45]. In this work, we do not *explicitly* address these latter issues, but instead focus on the intrinsic properties of $\varepsilon(k)$ and on the insights that can be derived from them. To support this analysis, we adopt the dressed ion theory (DIT) as a framework [34,46–51], which is an integral part of a unified treatment of electrolyte solutions,

ionic liquids, and polar fluids [23]. DIT, however, systematically incorporates the nonlinear contributions and excluded volume effects. Based on an exact formulation of statistical mechanics of liquids, DIT expresses the nonlinear effects in terms of “dressed particles,” and the linear part of the response in terms of $\varepsilon(k)$ or, equivalently, the screened Coulomb potential. A central part of the DIT analysis is the identification of the fundamental decay modes for electrostatic interactions and interparticle correlations—each mode having its own decay length and, if oscillatory, its own wavelength. This is an important ingredient in the present analysis.

Building on this framework, we perform a systematic study of the shape of the nonlocal dielectric function of electrolytic solutions across a broad range of electrolyte concentrations, using classical molecular dynamics simulations. The Bopp-Kornyshev-Sutmann scheme [52] is employed to accurately extract $\varepsilon(k)$, which is instrumental for avoiding the main sources of inaccuracy of results. Our main task will be threefold: (i) to unravel the interplay between the nonlocal dielectric response of the molecular solvent and the ionic subsystem and the corresponding modes of screening in electrolytes; (ii) to quantify the dominant decay modes of the pair correlation functions for the ionic components and their concentration dependence, whereby both the screened electrostatic interactions between ions and the interactional effects of ionic hydration are investigated; (iii) to assess the validity and limitations of the commonly used concept of a concentration-dependent dielectric constant, particularly for aqueous monovalent electrolytes.

The remainder of this paper is structured as follows. We will provide a concise overview of the principles and terminology (i) of nonlocal electrostatics (along with a summary of key constraints and anticipated features of the dielectric function) and (ii) of the dressed ion theory that will be used for the interpretation of the results. We then summarize the methodology of the MD simulations. In Sec. IV, we present our findings for the wave-number-dependent dielectric function and the electrolyte-concentration-dependent macroscopic dielectric permittivity of the solvent. We investigate the monotonic and the oscillatory decay modes of the electrostatic potential and pair correlations, whereby we make use of the theoretical framework of nonlocal electrostatics. Furthermore, we evaluate the decay lengths and wavelengths of the modes and rationalize those in terms of the dielectric function and the liquid structure. In the end, we summarize the main lessons of our findings.

II. BRIEF OVERVIEW OF NONLOCAL ELECTROSTATICS AND DRESSED ION THEORY

A. Basics of nonlocal electrostatics

1. Constitutive relation

An approach to account in electrostatics for the structure of a polarizable medium at the nanoscale is based on moving from the classical local constitutive relation between induction, $\mathbf{D}$, and electric field in the medium, $\mathbf{E}$, written as $\mathbf{D} = \varepsilon\mathbf{E}$, to a nonlocal tensorial form [53–55],

$$D^\alpha(\mathbf{r}) = \int d\mathbf{r}' \sum_\beta \varepsilon_{\alpha\beta}(\mathbf{r}, \mathbf{r}') E^\beta(\mathbf{r}'), \quad (1)$$

where α and β indices denote Cartesian components of the vector-fields and the integral is taken over the whole space. If $\rho^{\text{ext}}(\mathbf{r})$ is a fixed charge distribution that is immersed in the medium, then the Poisson equation is $\text{div} \mathbf{D}(\mathbf{r}) = -4\pi \rho^{\text{ext}}(\mathbf{r})$ (we use Gaussian units throughout the paper) and the electrostatic potential $\phi(\mathbf{r})$ created by $\rho^{\text{ext}}(\mathbf{r})$ is given by

$$\sum_{\alpha\beta} \frac{\partial}{\partial \mathbf{r}_\alpha} \int d\mathbf{r}' \varepsilon_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \frac{\partial \phi}{\partial \mathbf{r}'_\beta} = 4\pi \rho^{\text{ext}}(\mathbf{r}). \quad (2)$$

Here, $\rho^{\text{ext}}(\mathbf{r})$ is regarded as *external to the system* consisting of the dielectric medium. In a homogeneous medium, the dielectric tensor becomes translationally invariant, i.e., $\varepsilon_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \varepsilon_{\alpha\beta}(\mathbf{r} - \mathbf{r}')$ and then, Eq. (1) becomes local in Fourier space, i.e.,

$$D_{\mathbf{k}}^\alpha = \sum_{\beta} \varepsilon_{\alpha\beta}(\mathbf{k}) E_{\mathbf{k}}^\beta, \quad (3)$$

where

$$\mathbf{D}_{\mathbf{k}} = \int d\mathbf{r} \mathbf{D}(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}}, \quad (4)$$

and similarly, for $\varepsilon_{\alpha\beta}(\mathbf{k})$ and $\mathbf{E}_{\mathbf{k}}$. In a homogeneous and isotropic medium,

$$\varepsilon_{\alpha\beta}(\mathbf{k}) = \frac{k_\alpha k_\beta}{k^2} \varepsilon_{\parallel}(k) + \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2} \right) \varepsilon_{\perp}(k), \quad (5)$$

where $\varepsilon_{\parallel}(k)$ and $\varepsilon_{\perp}(k)$ are the longitudinal and transversal components of the dielectric tensor with respect to the vector $\mathbf{k}$. In electrostatics of such media, the Fourier component of the electric field has only longitudinal components, i.e. $\mathbf{E}_{\mathbf{k}} = E_k \hat{\mathbf{k}}$, where $k = |\mathbf{k}|$ and $\hat{\mathbf{k}} \equiv \frac{\mathbf{k}}{|\mathbf{k}|}$, and so is $\mathbf{D}_{\mathbf{k}}$. Thus, the constitutive relation reduces to

$$\mathbf{D}_{\mathbf{k}} = \varepsilon_{\parallel}(k) \mathbf{E}_{\mathbf{k}}. \quad (6)$$

The transversal component $\varepsilon_{\perp}(k)$ has no role for the electrostatic field at equilibrium and will therefore not be considered any further. The subscript $\parallel$ is often omitted for brevity, and $\varepsilon_{\parallel}(k) = \varepsilon(k)$ is called the wave-number-dependent dielectric function. $\mathbf{E}(\mathbf{r})$ consists of the electrostatic field from the external charge distribution $\rho^{\text{ext}}(\mathbf{r})$ and the induced polarization charge distribution of the medium. It is worth noting that these relationships are valid only when $\rho^{\text{ext}}(\mathbf{r})$ is sufficiently small so that the polarization response of the medium to a good approximation is linear.

2. Screened potential

In a homogeneous and isotropic medium, in linear response approximation, the generalized Poisson Eq. (2) in terms of Fourier components becomes

$$k^2 \varepsilon(k) \phi_{\mathbf{k}} = 4\pi \rho_{\mathbf{k}}^{\text{ext}}, \quad (7)$$

where $\rho_{\mathbf{k}}^{\text{ext}} = \int d\mathbf{r} \rho^{\text{ext}}(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}}$ and $\phi_{\mathbf{k}} = \int d\mathbf{r} \phi(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}}$. Hence, for small $\rho^{\text{ext}}(\mathbf{r})$, the potential in real space, $\phi(\mathbf{r})$, can be expressed as

$$\phi(\mathbf{r}) = \frac{1}{2\pi^2} \int d\mathbf{k} \frac{\rho_{\mathbf{k}}^{\text{ext}} e^{i\mathbf{k} \cdot \mathbf{r}}}{k^2 \varepsilon(k)} \quad (\text{linear response}). \quad (8)$$

To illustrate the implications of this relation, let us consider an electrostatic potential created by a point charge q located

at the coordinate origin with a small value, that is, $\rho^{\text{ext}}(\mathbf{r}) = q\delta(\mathbf{r})$ (where $\delta(\mathbf{r})$ is the Dirac δ function). For this case $\rho_{\mathbf{k}}^{\text{ext}} = q$ and substitution of this term into Eq. (8) will give an electrostatic potential $\phi_{(q)}(r)$ created at a radial distance r from this charge as

$$\phi_{(q)}(r) = q \frac{2}{\pi} \int_0^\infty \frac{dk}{\varepsilon(k)} \frac{\sin(kr)}{kr}. \quad (9)$$

For compactness and clarity, it can be written as $\phi_{(q)}(r) = q\varphi^*(r)$, where

$$\varphi^*(r) = \lim_{q \rightarrow 0} \frac{\phi_{(q)}(r)}{q} \quad (10)$$

is the (*unit*) *screened Coulomb potential* (note that hereafter the asterisk $*$ will not mean, as it is often used, complex conjugate; we use underbar for the latter). This function has a fundamental role in the theory of electrolytes, as it fully characterizes the medium's linear dielectric response to a fixed point-charge and is the Green's function for the screened potential. In Fourier space, the corresponding relation becomes

$$\varphi_k^* = \frac{4\pi}{k^2 \varepsilon(k)}. \quad (11)$$

Note that Eq. (8) can be recast into a convolution form in real space, as

$$\phi(\mathbf{r}) = \int d\mathbf{r}' \rho^{\text{ext}}(\mathbf{r}') \varphi^*(|\mathbf{r} - \mathbf{r}'|) \quad (\text{linear response}). \quad (12)$$

The properties of the function $\varepsilon(k)$, most importantly its zeros on the complex plane, determine the form of the resulting potential.

3. Classical limit in a nonconducting medium

In an isotropic dielectric medium, the classical, local electrostatic limit is recovered by neglecting the effect of spatial dispersion of the dielectric tensor: $\varepsilon_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \delta_{\alpha\beta} \delta(\mathbf{r} - \mathbf{r}') \varepsilon$. This translates into $\varepsilon(k) = \varepsilon(0) = \varepsilon$, where ε is the macroscopic dielectric constant of that medium. In this case, Eq. (9) will immediately give the Coulomb law, $\phi_{(q)}(r) = q/[\varepsilon r]$. But note that at long distances r , we always have the asymptotic result $\phi_{(q)}(r) \sim q/[\varepsilon r]$ in molecular polar liquids. This is valid for r much greater than any inverse values of the characteristic wave numbers that determine the variation of the function $\varepsilon(k)$. The situation is however more complicated in conducting media, where $\varepsilon(k) \rightarrow \infty$ when $k \rightarrow 0$. This case will be treated later.

4. Philosophy of nonlocal electrostatics

The central idea here has been to express electrostatics-related properties under study through $\varepsilon(k)$, if in the bulk, or $\varepsilon_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ in heterogeneous systems (including those containing interfaces), where both the longitudinal and transverse components of the dielectric tensor contribute to the screening, and then make use of some kind of modelling of these functions [56]. Dealing with $\varepsilon_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ necessitates to solve integrodifferential equation, and in some problems it was possible to obtain their analytical solutions (see, e.g., Refs. [57,58]) or express the relevant quantities through some moments of this function, extracting the values of these moments

through experimental data for those quantities. This was achieved, for instance, in retrieving the parameters of adsorption isotherms at the metal/electrolyte interface that can be expressed through those moments from experimental data for the interfacial capacitance determined by the same moments [59]. Approximate schemes, such as the so-called specular reflection approximation or dielectric approximation, attempt to relate the dielectric response of such inhomogeneous systems to the bulk function, and in those contexts, the transverse component may play a role [56].

This treatment of nonlocal electrostatics is an approximation that requires that the polarization response is linear. One can also extend it to a nonlinear response in dielectric media to a certain extent [43]. However, it is possible to formulate the exact statistical mechanics for polar fluids and electrolytes in terms of a formalism based on nonlocal electrostatics [49,51]. This approach results in a unified exact treatment of electrolyte solutions, ionic liquids, and polar fluids for both homogeneous and inhomogeneous systems [23], which will be utilized in the present work.

5. What do we know about $\varepsilon(k)$ of condensed dielectric media?

The interest in nonlocal dielectric function has a long history, first emerging in solid state physics, where the nonlocal dielectric function was calculated based on the microscopic theory [60], see in particular classical examples of Erenreich and Cohen [61] and Lindhard [62] that provided theoretical expressions for the dielectric functions of solids. In the context of polar liquids, water in particular, $\varepsilon(k)$ was put into the basis of *nonlocal electrostatics* of solutions [31], allowing one to capture the structural effect of the solvent on interionic interactions and solvation beyond the primitive or case-study models [63,64].

A series of works extended the use of this function to even describe inhomogeneous interfacial systems using model approximations expressing the interfacial complex dielectric tensor through $\varepsilon(k)$ see, e.g., Refs. [56,65–67]. More recently, renewed interest in $\varepsilon(k)$ has emerged in diverse areas such as the strongly correlated ionic and dipolar systems [20,30,45,68] and DNA biophysics [69–71], as well as the plasmonic response of low dimensional electronic systems such as graphene [72].

Most importantly, there are so far no direct experimental methods for measuring $\varepsilon(k)$. Information about it in solids is based on established microscopic first-principle models. In liquids, its basis is the fluctuation-dissipation theorem (FDT), which in classical statistical mechanics reads as

$$\chi(k) \equiv 1 - \frac{1}{\varepsilon(k)} = \frac{4\pi}{k^2} \frac{\Omega(k)}{k_B T}, \quad (13)$$

where $\chi(k)$ is the dielectric polarization response function, $\Omega(k)$ is the static charge-charge structure factor, defined as

$$\Omega(k) = \langle \hat{\rho}_{b,\mathbf{k}} \hat{\rho}_{b,-\mathbf{k}} \rangle, \quad (14)$$

$\hat{\rho}_{b,\mathbf{k}}$ is the Fourier transform of the microscopic, instantaneous bound charge density, and $\langle \dots \rangle$ stands for statistical averaging (see Appendix A). Thus, $\Omega(k)$ is the correlation function of the Fourier components of the fluctuations of the bound charge density of the medium. This is the simplest form

of FDT, which neglects quantum degrees of freedom of fluctuating bound charges; for more involved forms, see Ref. [73]. But for now, in this paper, the form of Eq. (13) will serve its purpose. The function $\Omega(k)$ can, in principle, be evaluated via neutron scattering measurements of atomic structure factors in the media and the known form-factors of charge distribution in the atoms [72,74–76], but the information so far obtained is rather limited and is incomplete in the small k domain. Thus, the main method here is MD simulations. Requiring very large simulation boxes, those so far have been performed only on the basis of a classical force-fields. For the results of such simulations for pure water, see Ref. [52] and the literature cited there. Molten salts were investigated in a pioneering Monte Carlo study by Tosi [77]. To the best of the authors' knowledge, the dielectric response of electrolytic solutions has not yet been systematically studied by simulations, with only limited work available [78].

Nevertheless, certain rigorous constraints on $\varepsilon(k)$ are well established. According to the Dolgov-Maximov-Kirzhnits theorem [60], $\varepsilon(k)$ can only be greater than 1 or smaller than 0, with a forbidden zone between 0 and 1. All known results of molecular simulations never got into that forbidden band. Obviously, at $k \rightarrow \infty$, $\varepsilon(k) \rightarrow 1$, i.e., $\chi(k) \rightarrow 0$ as no system can respond to a perturbation with infinitely large wave number. This limit is reached for wave numbers larger than any inverse characteristic scale of the $\varepsilon(k)$ variations. Not every simulation showed this, but some did [73,79]. Last, but not least, in a dielectric liquid, $\varepsilon(k \rightarrow 0)$ must reach the value of the macroscopic dielectric constant of the liquid (in simulations it should be the one that is obtained for the same model of form-factors and force-fields). However, in a system with ionic conductance, such as an electrolytic solution, $\varepsilon(k \rightarrow 0)$ diverges as $1/k^2$, which requires special treatment.

In a recent work by Becker *et al.*, [78] the dipolar contributions to the nonlocal dielectric response were studied by MD simulations of aqueous electrolytes. Their analysis was based on an extended Landau–Ginzburg field-theoretical framework, which incorporates higher-order gradient terms of the polarization field to account for overscreening effects and a quartic term to capture nonlinear dielectric saturation. They found that the influence of ions on the dielectric spectrum is negligible at large k and weak at intermediate k . Their study discussed the effect of ions on the water response, but the *direct* ionic contribution to the polarization response of the whole solution—particularly in the small- k regime—was not explicitly addressed. In this regime, as first analyzed by M. P. Tosi for molten salts [77], the ionic response leads to a characteristic divergence of the dielectric function, $\varepsilon(k) \propto k^{-2}$, when k goes to zero. This fundamental behavior of electrolyte systems, which is not contained in Becker *et al.*'s analysis of the dipolar polarization, has to be systematically explored, and this is what we do in the present paper.

B. Principles of the dressed ion theory

Here, we list some further considerations and basic formulas that we will later refer to in the interpretation of simulation data.

1. DIT at a glance

Consider a particle of species i in a homogeneous fluid. Let us place the origin of the coordinate system at its center with the coordinate axes fixed to the particle. In the surroundings of the particle, the distribution of j particles is described by the pair distribution function g_{ij} that contains information about their positions and orientations relative to that of the central i particle, which has a fixed orientation relative to the coordinate system. The orientation variable will not be explicitly shown unless it is needed. The deviation in the number density of j particles from their bulk density n_j is equal to $n_j h_{ij}$, where $h_{ij} = g_{ij} - 1$ (if the i and j particles have spherical symmetry, g_{ij} is the “radial distribution function” that depends only on r). This deviation gives rise to a charge density $\rho_i^{\text{cloud}}(\mathbf{r})$ around the particle. In electrolytes, this charge density is commonly called the “ion cloud” of the i particle, but $\rho_i^{\text{cloud}}(\mathbf{r})$ also contains the contributions of oriented solvent molecules. It is determined by all kinds of interactions between the central i particle and the rest, that is, not only by the electrostatic interactions. The polarization charge density due to electrostatic interactions is a part of $\rho_i^{\text{cloud}}(\mathbf{r})$ and can be obtained using linear response when these interactions are weak. However, close to the central ion, the interactions are often strong, and nonlinear contributions are important.

In the general case, the mean electrostatic potential $\phi_i(\mathbf{r})$ due to the central i particle, is given by the Coulomb potential formula

$$\phi_i(\mathbf{r}) = \int d\mathbf{r}' \rho_i^{\text{tot}}(\mathbf{r}') \varphi(|\mathbf{r} - \mathbf{r}'|), \quad (15)$$

where $\rho_i^{\text{tot}} = \rho_i^{\text{int}} + \rho_i^{\text{cloud}}$ is the total charge density of the i particle itself and its cloud, ρ_i^{int} is the internal charge density of the particle (ρ_i^{int} would have played a role of ρ^{ext} in Eq. (12) of the linear response theory), and $\varphi(r) = 1/r$ is the Coulomb potential in vacuum. The bare charge of the particle is $q_i = \int d\mathbf{r} \rho_i^{\text{int}}(\mathbf{r})$ and its dipole moment is $\boldsymbol{\mu}_i = \int d\mathbf{r} \mathbf{r} \rho_i^{\text{int}}(\mathbf{r})$. In Fourier space, Eq. (15) becomes $\phi_{i,\mathbf{k}} = \rho_{i,\mathbf{k}}^{\text{tot}} \varphi_k$, where $\varphi_k = 4\pi/k^2$, that is, the Fourier transform of $\varphi(r)$. Note that ρ_i^{tot} and ρ_i^{cloud} are average charge densities that result from interparticle correlations, while ρ^{ext} in Eq. (12) is a fixed, external charge density. One can regard ρ_i^{cloud} as the total polarization response due to the i particle caused by both its electrostatic and nonelectrostatic interactions with the surrounding particles. The net charge of ρ_i^{tot} is zero due to local electroneutrality, $\int d\mathbf{r} \rho_i^{\text{tot}}(\mathbf{r}) = 0$, so the net charge of the cloud is $\int d\mathbf{r} \rho_i^{\text{cloud}}(\mathbf{r}) = -q_i$.

Let us now formally rewrite

$$\phi_{i,\mathbf{k}} = \rho_{i,\mathbf{k}}^{\text{tot}} \varphi_k = \rho_{i,\mathbf{k}}^* \varphi_k^*, \quad (16)$$

where we have introduced $\rho_{i,\mathbf{k}}^* = \rho_{i,\mathbf{k}}^{\text{tot}} \varepsilon(k)$ and used the fact that the screened Coulomb potential is related to the Fourier component of the potential in vacuum as $\varphi_k^* = \varphi_k / \varepsilon(k)$. This implies that we have

$$\phi_i(\mathbf{r}) = \int d\mathbf{r}' \rho_i^*(\mathbf{r}') \varphi^*(|\mathbf{r} - \mathbf{r}'|). \quad (17)$$

The form of Eq. (17) is similar to that of Eq. (12). The difference is that $\rho^{\text{ext}}(\mathbf{r}')$ in Eq. (12) is a fixed charge density, external to the system consisting of the fluid, while $\rho_i^*(\mathbf{r}')$ is

a charge density associated with a particle of the system, see below. Furthermore, Eq. (12) is valid only when $\rho^{\text{ext}}(\mathbf{r}')$ is small enough so that the linear response is appropriate, while Eq. (17) is formally exact, valid in the general case where nonlinear response may be important.

The entity $\rho_i^*(\mathbf{r}')$ is the charge density of a *dressed particle* (or a *dressed ion* when $q_i \neq 0$) of species i [46,47]. This charge density minus the internal one, $\rho_i^*(\mathbf{r}) - \rho_i^{\text{int}}(\mathbf{r}) \equiv \rho_i^{\text{dress}}(\mathbf{r})$, constitutes the “dress,” which contains the nonlinear part of electrostatic polarization response due to the i particle, see Appendix B. The linear part of the polarization response is taken care of by $\varphi^*(r)$ via its dependence on the dielectric function $\varepsilon(k)$. Equation (17) is the *screened version of the Coulomb potential formula* Eq. (15) [$\phi_i(\mathbf{r})$ is the same in both equations].

In electrolytes, the dress has a nonzero net charge, while its charge is zero in a pure solvent because all particles in the dress are electroneutral in the latter case. Therefore, the total charge q_i^* of a dressed i particle, $q_i^* = \int d\mathbf{r} \rho_i^*(\mathbf{r})$, goes to the bare charge q_i when the electrolyte concentration goes to zero. Note that $\int d\mathbf{r} \rho_i^{\text{dress}}(\mathbf{r}) \neq \int d\mathbf{r} \rho_i^{\text{cloud}}(\mathbf{r})$ because ρ_i^{cloud} and ρ_i^{dress} differ by the linear electrostatic polarization response due to the i particle, see Appendix B for details.

2. Ionic contributions to the nonlocal dielectric function

The entity ρ_i^* has a fundamental role in the theory of electrolytes and polar fluids. For example, one can show that $\varepsilon(k)$ can be explicitly expressed in terms of it, [47] namely:

$$\varepsilon(k) = 1 - \frac{4\pi \Lambda^*(k)}{k^2}, \quad (18)$$

where

$$\Lambda^*(k) = -\frac{1}{k_B T} \sum_j n_j \langle \rho_{j,\mathbf{k}}^{\text{int}} \rho_{j,-\mathbf{k}}^* \rangle_\theta, \quad (19)$$

$\langle \cdot \rangle_\theta$ denotes the average over the orientation θ of the j particle, and n_j is the number density of species j . The function Λ^* is a kind of polarization response function with the following properties. Let ρ^{pol} be the polarization charge-density caused by a weak external charge-density ρ^{ext} . The resulting total electrostatic potential ϕ is, as we have seen, given by $\phi_{\mathbf{k}} = \rho_{\mathbf{k}}^{\text{ext}} \varphi_k^* = \rho_{\mathbf{k}}^{\text{ext}} \varphi_k / \varepsilon(k)$. One can show that $\rho_{\mathbf{k}}^{\text{pol}} = \Lambda^*(k) \phi_{\mathbf{k}}$, that is, Λ^* is the linear response function that gives ρ^{pol} as the polarization response to the total potential ϕ . This is done in Appendix B, where the relationship between Eqs. (18) and (19), on the one hand, and Eq. (13), on the other hand, are discussed. It is thereby shown that the two expressions (13) and (18) for $\varepsilon(k)$ are equivalent to each other.

This formalism helps to highlight features of $\varepsilon(k)$ in conducting media. As pointed out earlier, in electrolyte solutions $\varepsilon(k \rightarrow 0)$ diverges as $1/k^2$, a divergence known as “perfect screening.” Eq. (18) can be rewritten as

$$\varepsilon(k) = 1 - \frac{4\pi \Lambda^*(0)}{k^2} - \frac{4\pi [\Lambda^*(k) - \Lambda^*(0)]}{k^2}, \quad (20)$$

where the last term stays finite when $k \rightarrow 0$ because the MacLaurin expansion of $\Lambda^*(k)$ lacks the term linear in k , being the Fourier transform of a function that has radial

symmetry in ordinary space. Equation (19) implies that [49]

$$\Lambda^*(k=0) = -\frac{1}{k_B T} \sum_j n_j q_j q_j^*, \quad (21)$$

where we have used the fact that $q_j^* = [\rho_{j,\mathbf{k}}^*]_{k=0} = \int d\mathbf{r} \rho_j^*(\mathbf{r})$ (note that $q_j = [\rho_{j,\mathbf{k}}^{\text{int}}]_{k=0}$). Thus, we have [49]

$$\varepsilon(k) = \varepsilon_{\text{sing}}(k) + \varepsilon_{\text{reg}}(k) = \frac{4\pi}{k_B T} \sum_j n_j q_j q_j^* \frac{1}{k^2} + \varepsilon_{\text{reg}}(k), \quad (22)$$

where $\varepsilon_{\text{sing}}(k)$ is the singular part of the dielectric function that diverges like $1/k^2$ when $k \rightarrow 0$ and $\varepsilon_{\text{reg}}(k)$ is the regular part:

$$\varepsilon_{\text{reg}}(k) = 1 - \frac{4\pi[\Lambda^*(k) - \Lambda^*(0)]}{k^2}, \quad (23)$$

which is finite at $k = 0$. For a pure polar fluid (without any ions), $\varepsilon_{\text{sing}}(k)$ is identically equal to zero because $q_i = 0$ for all species. Since $\varepsilon(k) = \varepsilon_{\text{reg}}(k)$ in this case, we have $\varepsilon_{\text{reg}}(0) = \varepsilon(0) = \varepsilon$, i.e., the dielectric constant.

For electrolyte solutions at very low concentrations, the approximations $\varepsilon_{\text{reg}}(k) \approx \varepsilon_{\text{solv}}(k)$ and $q_j^* \approx q_j$ are valid, where $\varepsilon_{\text{solv}}(k)$ is the dielectric function for the pure polar solvent. As

$$\frac{4\pi}{k_B T} \sum_j n_j q_j^2 = \kappa_{D,0}^2 \quad (24)$$

($\kappa_{D,0}$ is the so-called “inverse Debye length in vacuum”), we get then

$$\varepsilon(k) \approx \varepsilon_{\text{solv}}(k) + \kappa_{D,0}^2/k^2. \quad (25)$$

This approximate expression was originally introduced as an interpolation formula in Ref. [80], intended for cases where the electrolyte is so diluted that the Debye length is significantly greater than any characteristic inverse wave numbers of the function $\varepsilon_{\text{solv}}(k)$. It is now understood that this formula, rather than being merely an approximation, represents an exact limiting law.

The presence of the singular part of $\varepsilon(k)$ constitutes a very important effect of the presence of ions. It plays a dominant role for low concentrations, leading to the exponential screening of electrostatic interactions in electrolytes. At higher concentrations, there are also considerable ionic contributions in the regular part. A central question that we will deal with in this work is: What effects of the ions are important in the latter?

3. Screening of the electrostatic potential—Debye screening and beyond

The screened Coulomb potential $\varphi^*(r)$ is in Fourier space defined by Eq. (11) and by inserting Eq. (22) we obtain [49,50]

$$\varphi_{\mathbf{k}}^* = \frac{4\pi}{k^2 \varepsilon(k)} = \frac{4\pi}{k_B T \sum_j n_j q_j q_j^* + k^2 \varepsilon_{\text{reg}}(k)}. \quad (26)$$

Let us consider an electrolyte solution. Each simple pole of $\varphi_{\mathbf{k}}^*$ in complex k space, that is, each simple zero of the denominator, gives a contribution to $\varphi^*(r)$ that decays like a Yukawa function $e^{-\kappa_\nu r}/r$, where κ_ν is the solution to the equation $\varepsilon(i\kappa_\nu) = 0$ and i is the imaginary unit (this is a consequence of Cauchy’s residue theorem in complex analysis). This equation

has multiple solutions $i\kappa_\nu$, $\nu = 1, 2, 3, \dots$, and each solution gives a *decay mode* for the electrostatic potential with a different decay parameter κ_ν in the Yukawa function contribution. In dilute electrolyte solutions, such analysis was performed in Ref. [80] for the limiting form of $\varepsilon(k)$, Eq. (25). Let us proceed with it for the general case.

Consider the zero of $\varepsilon(i\kappa_\nu)$ with the smallest κ_ν value, $\kappa = \kappa_1$. It gives the longest decay length $\lambda = 1/\kappa$ of $\varphi^*(r)$, which therefore has a leading Yukawa function contribution that decays when $r \rightarrow \infty$ as

$$\varphi^*(r) \sim \frac{e^{-\kappa r}}{\mathcal{E}^{\text{eff}}(\kappa) r}, \quad (27)$$

where $\mathcal{E}^{\text{eff}}(\kappa) = \varepsilon_{\text{reg}}(i\kappa) + i\kappa \varepsilon'_{\text{reg}}(i\kappa)/2$ is an effective dielectric permittivity and $\varepsilon'_{\text{reg}}(k) = d\varepsilon_{\text{reg}}(k)/dk$, cf. Ref. [80] (this expression for $\mathcal{E}^{\text{eff}}(\kappa)$ follows from Cauchy’s theorem).

The equation $\varepsilon(i\kappa_\nu) = 0$ can be expressed as

$$\left[\frac{4\pi}{k_B T} \sum_j n_j q_j q_j^* + k^2 \varepsilon_{\text{reg}}(k) \right]_{k=i\kappa_\nu} = 0. \quad (28)$$

For electrolytes, where the first term is nonzero, this is the same as [50]

$$\kappa_\nu^2 = \frac{4\pi}{k_B T \mathcal{E}^*(\kappa_\nu)} \sum_j n_j q_j q_j^* \quad (\text{only for electrolytes}), \quad (29)$$

where $\mathcal{E}^*(\kappa_\nu) = \varepsilon_{\text{reg}}(i\kappa_\nu)$ is called the *dielectric factor*. Equation (29) is an equation for the unknown κ_ν since it occurs on both sides. The set of solutions κ_ν constitutes the decay parameters for the various decay modes. Note that on the right-hand side, only $\mathcal{E}^*(\kappa_\nu)$ depends on κ_ν . The existence of several decay modes is therefore directly linked to the fact that the dielectric factor has different values for the different modes.

When the concentration goes to zero, $\kappa = \kappa_1$ goes to zero, $q_j^* \rightarrow q_j$ and $\mathcal{E}^*(\kappa) \rightarrow \varepsilon_{\text{reg}}(0) \rightarrow \varepsilon_{\text{solv}}(0) = \varepsilon$, whereby the expression (29) for $\kappa = \kappa_1$ goes over to the usual definition of the Debye parameter κ_D ,

$$\kappa_D^2 = \frac{4\pi}{k_B T \varepsilon} \sum_j n_j q_j^2, \quad (30)$$

where ε is the dielectric constant of the pure solvent. Furthermore, $\mathcal{E}^{\text{eff}}(\kappa) \rightarrow \varepsilon$ so we recover the usual Debye-Hückel (DH) expression for the screened Coulomb potential for electrolytes $\varphi^*(r) \sim e^{-\kappa_D r}/[\varepsilon r]$, which is quite accurate for large r in sufficiently dilute solutions. Note that the exact expression (29) for $\kappa = \kappa_1$ differs from the traditional definition (30) of the Debye parameter κ_D only by the occurrence of $q_j q_j^*$ instead of q_j^2 and $\mathcal{E}^*(\kappa)$ instead of ε . In the DH approximation there is only one decay length, the Debye length $\lambda_D = 1/\kappa_D$, while in exact theory, there is a set of different decay lengths, one for each decay mode. It is only for the leading mode at low concentrations that $\mathcal{E}^*(\kappa)$ is approximately equal to the dielectric constant ε . For all other modes, the values of $\mathcal{E}^*(\kappa_\nu)$ are entirely different.

In pure polar solvent $\kappa = 0$ and we obtain $\varphi^*(r) \sim 1/[\varepsilon r]$, as mentioned earlier. However, the other solutions to $\varepsilon(i\kappa_\nu) = 0$ with $\nu = 2, 3, \dots$, that is, the other decay modes, give

additional contributions to $\varphi^*(r)$ that we will treat later. They are very important in both pure polar fluids and solutions, also in very dilute ones.

When the intermolecular potentials include dispersion interactions that decay as $1/r^6$ —such as the Lennard-Jones terms used in our simulations—the screened Coulomb potential and the pair correlation functions develop additional long-range contributions. They decay as power laws of the form $1/r^\nu$ with $\nu \geq 6$. Such power-law screening was first identified in quantum mechanical treatments of ionic systems [81,82], but it also arises in classical statistical mechanics of electrolytes, when $1/r^6$ dispersion interactions are present as shown by both formal analysis and simulations [83–85]. Importantly, power-law terms decay more slowly with r than any exponentially decaying term. This means that, at sufficiently large distances, the electrostatic potential in electrolytes falls off as $1/r^6$ [83].

The physical origin of this effect is that dispersion forces are not screened. Since the strengths of the total anion-anion and anion-cation interactions differ at large separations due to dispersion forces, a residual imbalance develops, giving rise to a charge distribution that extends far from each ion. In practice, however, the amplitudes of these power-law terms are small in incompressible fluids. For most distances of interest, the exponential (Yukawa) decay dominates, and the power-law tail only becomes visible at very large separations [86,87]. Therefore, in the present work, we analyze our simulation results using the Yukawa form, Eq. (27), as the effective decay-law for $\varphi^*(r)$, while avoiding the regime of very large r values where the power-law tails would take over. This will be done in the present work in the analysis of the decay of all functions.

The mean electrostatic potential $\phi_i(\mathbf{r})$ due to an i particle placed with some fixed orientation at the origin is given by Eqs. (15) and (17). In Fourier space ϕ_i is given by the expression in Eq. (16). From the right-hand side of the latter and Eq. (26) it follows that

$$\phi_{i,\mathbf{k}} = \rho_{i,\mathbf{k}}^* \varphi_{\mathbf{k}}^* = \frac{4\pi \rho_{i,\mathbf{k}}^*}{k^2 \varepsilon(k)} = \frac{4\pi \rho_{i,\mathbf{k}}^*}{\frac{4\pi}{k_B T} \sum_i n_i q_i q_i^* + k^2 \varepsilon_{\text{reg}}(k)}. \quad (31)$$

Like before, the solutions to the equation $\varepsilon(i\kappa_\nu) = 0$ or, equivalently Eq. (29), give the decay modes. For spherical i particles like simple ions, this implies that in dilute solutions the mean electrostatic potential decays when $r \rightarrow \infty$ like [34,46,47],

$$\phi_i(r) \sim \frac{q_i^{\text{eff}}(\kappa) e^{-\kappa r}}{\mathcal{E}^{\text{eff}}(\kappa) r}, \quad (32)$$

where $q_i^{\text{eff}}(\kappa) = \rho_{i,\mathbf{k}}^*|_{\mathbf{k}=\kappa\mathbf{r}} = \int d\mathbf{r} \rho_i^*(r) \sinh(\kappa r)/[\kappa r]$ is an effective ionic charge. This expression is obtained from the numerator of Eq. (31) evaluated at $k = i\kappa$. Note that $q_i^{\text{eff}}(\kappa)$ is different from q_i^* which is independent of κ . The concept of a κ -dependent effective charge is, in fact, present already in the Debye-Hückel theory for electrolytes, where $q_i^{\text{eff}}(\kappa_D) = e^{\kappa_D d}/[1 + \kappa_D d]$ and d is the ionic diameter. In that case $\mathcal{E}^{\text{eff}}(\kappa)$ and $\mathcal{E}^*(\kappa)$ are approximated by ε and q_i^* by q_i , as we have seen. For nonspherical particles the effective charge in Eq. (32) is replaced by a direction-dependent quantity that

is given by $\rho_{i,\mathbf{k}}^*|_{\mathbf{k}=\kappa\mathbf{r}}$, see Ref. [48] for details. It is a kind of “multipolar effective charge.”

The pair correlation function between simple ions decays like [34,46,47]

$$h_{ij}(r) \sim -\frac{q_i^{\text{eff}}(\kappa) q_j^{\text{eff}}(\kappa) e^{-\kappa r}}{k_B T \mathcal{E}^{\text{eff}}(\kappa) r} \quad (33)$$

when $r \rightarrow \infty$. The right-hand side is the same as $-1/k_B T$ times the leading term of $q_j^{\text{eff}}(\kappa) \phi_i(r)$ and $q_i^{\text{eff}}(\kappa) \phi_j(r)$, that is, the interaction energy between the mean electrostatic potential from one ion and the effective charge of the other. For nonspherical particles, the effective charge of each particle is replaced by the same multipolar effective charge as in $\phi_i(\mathbf{r})$ [48].

In addition to the leading asymptotic term for large r with decay length $1/\kappa$ shown above, there are other contributions to the various functions that have shorter decay lengths, for example, terms that decay like $f(r)e^{-2\kappa r}/r^2$, where $f(r)$ is a slowly varying function with r [46,88]. They arise because of the inherent nonlinearity of the theory and the effects of many-body correlations, see also Ref. [23].

4. Full picture of the decay modes

Let us now consider all decay modes. Each of them gives the same kind of contribution as the leading term shown above, but with a different value of κ_ν that is a solution to $\varepsilon(i\kappa_\nu) = 0$ and, equivalently, to Eq. (29). For example,

$$\varphi^*(r) = \frac{e^{-\kappa_1 r}}{\mathcal{E}^{\text{eff}}(\kappa_1) r} + \frac{e^{-\kappa_2 r}}{\mathcal{E}^{\text{eff}}(\kappa_2) r} + \frac{e^{-\kappa_3 r}}{\mathcal{E}^{\text{eff}}(\kappa_3) r} + \dots, \quad (34)$$

where we have shown only the Yukawa function terms (as mentioned above, there are also short-range contributions with other functional forms, but the Yukawa terms are often the most important ones, at least for large r). Likewise, the mean potential due to an i particle has the same Yukawa function terms. For a spherical particle, it is [50,88]

$$\phi_i(r) = \frac{q_i^{\text{eff}}(\kappa_1) e^{-\kappa_1 r}}{\mathcal{E}^{\text{eff}}(\kappa_1) r} + \frac{q_i^{\text{eff}}(\kappa_2) e^{-\kappa_2 r}}{\mathcal{E}^{\text{eff}}(\kappa_2) r} + \frac{q_i^{\text{eff}}(\kappa_3) e^{-\kappa_3 r}}{\mathcal{E}^{\text{eff}}(\kappa_3) r} + \dots, \quad (35)$$

where each mode has its own value of the effective charge.

A solution to $\varepsilon(i\kappa_\nu) = 0$ can be complex-valued, say, $\kappa_2 = \kappa_2^{\text{Re}} + i\kappa_2^{\text{Im}}$, where κ_2^{Re} and κ_2^{Im} are the real and imaginary parts, respectively. Thereby, the complex conjugate κ_2 must also be a solution, say, $\kappa_3 = \kappa_2 = \kappa_2^{\text{Re}} - i\kappa_2^{\text{Im}}$ and this pair of contributions to Eq. (34) forms an exponentially damped oscillatory term. Then Eq. (34) can be written as

$$\varphi^*(r) = \frac{e^{-\kappa_1 r}}{\mathcal{E}^{\text{eff}}(\kappa_1) r} + \frac{2 e^{-\kappa_2^{\text{Re}} r}}{|\mathcal{E}^{\text{eff}}(\kappa_2)| r} \cos(\kappa_2^{\text{Im}} r + \gamma(\kappa_2)) + \dots, \quad (36)$$

where $\gamma(\kappa_2) = \text{Arg}(\mathcal{E}^{\text{eff}}(\kappa_2))$ [the symbol $\text{Arg}(\cdot)$ stands for the argument of the complex number]. The function in the second term will be denoted as an “oscillatory Yukawa function.” The mean electrostatic potential ϕ_i also have the corresponding oscillatory contributions. At high electrolyte

concentrations the decay parameter κ_1 can also be complex-valued and form an exponentially damped oscillatory term together with an additional solution to $\varepsilon(i\kappa_\nu) = 0$. This occurs at concentrations higher than the so-called Kirkwood cross-over point, [32,89] named after Kirkwood who obtained it in a primitive model theory of electrolytes [90,91].

For a pure polar fluid, where $\kappa = \kappa_1 = 0$, Eq. (36) becomes

$$\varphi^*(r) = \frac{1}{\varepsilon r} + \frac{2 e^{-\kappa_2^{\text{Re}} r}}{|\mathcal{E}^{\text{eff}}(\kappa_2)| r} \cos(\kappa_2^{\text{Im}} r + \gamma(\kappa_2)) + \dots \quad (37)$$

This form of $\varphi^*(r)$ for polar fluids have been obtained in approximate theories [79]. In the absence of ions, the equation $\varepsilon(i\kappa_\nu) = 0$ becomes $\varepsilon_{\text{reg}}(i\kappa_\nu) = 0$, which we can also express as $\mathcal{E}^*(\kappa_\nu) = 0$. For electrolyte solutions this implies that the dielectric factor goes to zero for the decay modes with κ_ν for $\nu \geq 2$ when the ionic concentration goes to zero. Note that the DH-like expression for κ_ν , Eq. (29), is valid only for electrolytes.

The pair correlation function h_{ij} has the same decay modes as $\varphi^*(r)$ in the overwhelming majority of cases (the only exceptions are charge-inversion invariant model systems that remain the same when all charges reverse their signs, see Refs. [50,51]—all realistic model systems are *not* charge-inversion invariant). All decay modes give contributions to the correlation functions between all kinds of particles in the system, that is, the water-water, water-ion and ion-ion correlations all have the same decay lengths and, for the oscillatory modes, the same wavelengths. The magnitude of each mode can, however, be very different for different pairs of i and j because it is determined by the values of the effective charges of the species involved. Since the effective charges have different values for the different modes, one mode can be large for some species but small for some other species, while it may be the other way around for another mode.

All decay modes, each corresponding to a monotonic or an oscillatory Yukawa function in the electrostatic potential and the pair correlation functions, are solutions to $\varepsilon(i\kappa_\nu) = 0$, irrespective of whether they are dominated by electrostatic or structural correlations, as shown in the DIT analysis [50,51]. This nontrivial fact, which does not hold for charge-inversion invariant systems (see next section), is a consequence of the coupling between density-density and charge-charge correlations. Therefore, all contributions that decay like Yukawa functions for the present system can, in principle, be obtained by analyzing the solutions of $\varepsilon(i\kappa_\nu) = 0$.

5. Decay modes and the ion-ion correlation functions

For the ion-ion correlations in the aqueous solutions, we have analogously to Eq. (35)

$$h_{ij}(r) = - \frac{q_i^{\text{eff}}(\kappa_1) q_j^{\text{eff}}(\kappa_1) e^{-\kappa_1 r}}{k_B T \mathcal{E}^{\text{eff}}(\kappa_1) r} - \frac{q_i^{\text{eff}}(\kappa_2) q_j^{\text{eff}}(\kappa_2) e^{-\kappa_2 r}}{k_B T \mathcal{E}^{\text{eff}}(\kappa_2) r} - \dots, \quad (38)$$

where we have only shown the Yukawa function terms (again, there are also contributions with different functional forms that have a shorter range than the first term).

It is also illuminating to study the ionic contributions to the charge-charge (QQ), density-density (NN), and density-charge (NQ) correlation functions. For binary electrolytes with ions of equal but opposite charges, they are proportional to

$$\begin{aligned} h_{\text{QQ}}^{\text{ions}}(r) &= \frac{1}{4} [h_{++}(r) + h_{--}(r) - 2h_{+-}(r)], \\ h_{\text{NN}}^{\text{ions}}(r) &= \frac{1}{4} [h_{++}(r) + h_{--}(r) + 2h_{+-}(r)], \\ h_{\text{NQ}}^{\text{ions}}(r) &= \frac{1}{4} [h_{++}(r) - h_{--}(r)]. \end{aligned} \quad (39)$$

These three functions fully characterize the pair distributions of the ions in binary electrolytes because

$$h_{ij}(r) = h_{\text{NN}}^{\text{ions}}(r) + h_{\text{NQ}}^{\text{ions}}(r) [q_i + q_j] / q + h_{\text{QQ}}^{\text{ions}}(r) q_i q_j / q^2, \quad (40)$$

where $q = q_+ = -q_-$. The Yukawa terms of $h_{\text{IJ}}^{\text{ions}}$ for IJ = QQ, NN, and NQ are

$$\begin{aligned} h_{\text{IJ}}^{\text{ions}}(r) &= - \frac{q_i^{\text{eff}}(\kappa_1) q_j^{\text{eff}}(\kappa_1) e^{-\kappa_1 r}}{k_B T \mathcal{E}^{\text{eff}}(\kappa_1) r} \\ &\quad - \frac{q_i^{\text{eff}}(\kappa_2) q_j^{\text{eff}}(\kappa_2) e^{-\kappa_2 r}}{k_B T \mathcal{E}^{\text{eff}}(\kappa_2) r} - \dots, \end{aligned} \quad (41)$$

where $q_{\text{O}}^{\text{eff}} = [q_+^{\text{eff}} - q_-^{\text{eff}}] / 2$ and $q_{\text{N}}^{\text{eff}} = [q_+^{\text{eff}} + q_-^{\text{eff}}] / 2$. We see that all these functions have the same decay parameters κ_ν .

Again, when some κ_ν are complex-valued, the ion-ion correlations have oscillatory contributions, like in Eq. (36),

$$\begin{aligned} h_{\text{IJ}}^{\text{ions}}(r) &= - \frac{q_i^{\text{eff}}(\kappa_1) q_j^{\text{eff}}(\kappa_1) e^{-\kappa_1 r}}{k_B T \mathcal{E}^{\text{eff}}(\kappa_1) r} \\ &\quad - \frac{2 |q_i^{\text{eff}}(\kappa_2) q_j^{\text{eff}}(\kappa_2)| e^{-\kappa_2^{\text{Re}} r}}{k_B T |\mathcal{E}^{\text{eff}}(\kappa_2)| r} \\ &\quad \times \cos(\kappa_2^{\text{Im}} r + \vartheta_{\text{IJ}}(\kappa_2)) - \dots, \end{aligned} \quad (42)$$

where $\vartheta_{\text{IJ}} = \text{Arg}(\mathcal{E}^{\text{eff}}) - \text{Arg}(q_i^{\text{eff}}) - \text{Arg}(q_j^{\text{eff}})$. For $h_{ij}(r)$ we have the analogous expression.

For completeness, we mention the following facts for charge-inversion invariant model systems. In such systems, the density-charge correlations are identically equal to zero, so $h_{\text{NQ}}^{\text{ions}}(r) \equiv 0$. As a consequence of this, there are modes with Yukawa function decay that are *not* zeros of $\varepsilon(k)$. For example, the decay modes of $h_{\text{NN}}^{\text{ions}}(r)$ are different from those of $h_{\text{QQ}}^{\text{ions}}(r)$ [50,51]. Only the latter are given by the solution to $\varepsilon(i\kappa_\nu) = 0$. An example is the restricted primitive model of electrolytes, where the anions and cations have the same size and only differ in the sign of their charges. Realistic models are not charge-inversion invariant, but when anions and cations in symmetric electrolytes have nearly the same size, $h_{\text{NQ}}^{\text{ions}}(r)$ is nonzero but small since the electrolyte is nearly invariant. For the system that we study in the present work, both ions and solvent contribute to $h_{\text{NQ}}^{\text{ions}}(r)$ because neither the electrolyte nor the solvent has such invariance.

III. COMPUTATIONAL MODEL AND PROCEDURE

All simulations have been performed with the MD package GROMACS [92]. The SPC/E model was used to mimic the water molecule [93], and ions were modelled with the OPLS force field [94]. In each simulation, periodic boundary conditions were applied in all three spatial directions. To investigate

the dependence of the nonlocal dielectric response on electrolyte concentration, simulations were performed for pure water and aqueous electrolytes with concentrations ranging from 10 mM to 3.60 M. Each system comprised 333 300 water molecules and a concentration-dependent number of ion pairs (see the Supplemental Material [95] for details of simulation setup).

The temperature was controlled through the Nose-Hoover thermostat at 298 K with a coupling constant of 1.0 ps. A cutoff distance of 1.2 nm was applied for the van der Waals interactions using direct summation. Long-range electrostatic interactions were calculated using the particle mesh Ewald (PME) method, with a fast Fourier transform (FFT) grid spacing of 0.1 nm and cubic interpolation for the reciprocal space. A cutoff length of 1.2 nm was also employed for the short-range contributions to the electrostatic interactions in real space. The equations of motion were integrated using the leapfrog algorithm with a time step of 2 fs. For each simulation, the system was initially equilibrated under the NPT ensemble with 1 bar for 10 ns to ensure stability. Subsequently, simulations were switched to the NVT ensemble. Following equilibration, a 5 ns production run was performed for data analysis. To ensure the robustness of the results, each system was simulated 20 times with different initial configurations.

From the simulation trajectories, we computed the microscopic, instantaneous charge density in real space, followed by a Fourier transform to obtain the charge-charge structure factor $\Omega(k)$ following Eq. (14). Owing to the large-scale aqueous electrolyte systems, we developed a custom optimized analysis tool based on MD Analysis in Python, allowing the evaluation of direct FFT on the graphics processing unit (GPU). This tool is specifically designed to enable efficient computation of the structure factor using direct FFT operations on GPU, significantly improving computational performance for large datasets.

IV. RESULTS AND DISCUSSION

A. Dielectric response function

Our starting point is the nonlocal wavevector-dependent response function, $\chi(k)$, derived from MD simulation based on Eq. (13). Consistent with previous computational results for pure water [52], as depicted in Fig. 1, an over-response ($\chi(k) > 1$) is observed over the range of $k \approx 0.3 \text{ \AA}^{-1}$ – $16 \text{ \AA}^{-1}$. This interval corresponds to the wavelength that align with a damped structural periodicity in water. Such behavior indicates a resonance between the Fourier components of the external field and the bound charge density, suggesting a pronounced dielectric overscreening effect. Specifically, $\chi(k)$ exhibits distinct features, including a prominent peak ($k \approx 3.0 \text{ \AA}^{-1}$) and a shoulder ($k \approx 5.0 \text{ \AA}^{-1}$), attributed to intermolecular structural organisation (Fig. S2 in the Supplemental Material [95], where the various contributions to $\chi(k)$ are plotted). These features correspond, respectively, to real-space distances of $\approx 0.21 \text{ nm}$ and $\approx 0.12 \text{ nm}$, and are primarily attributed to intermolecular correlations involving O-O, O-H, and H-H interactions (as shown in Fig. S3 in the Supplemental Material) [79,95].

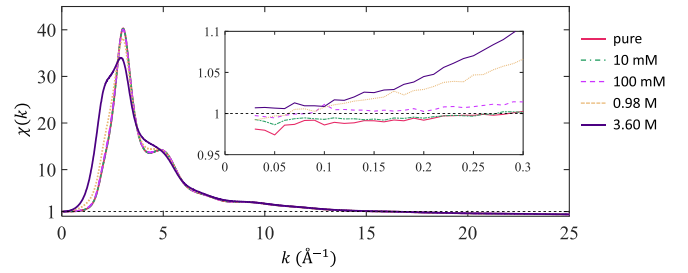


FIG. 1. MD-based results for dielectric polarization response function, $\chi(k)$, of pure water and the aqueous electrolyte plotted for the indicated NaCl concentrations. This function is calculated from $\chi(k) = 4\pi\Omega(k)/[k_B T k^2]$, with the charge-charge structure factor $\Omega(k)$ obtained from the simulated charge-density correlation function based on Eq. (14). The black dashed line marks $\chi = 1$. Inset shows $\chi(k)$ for small wave numbers k .

Interestingly, the response function demonstrates practically no concentration dependence in dilute electrolytes (from 10 mM to 0.98 M) in the moderate to large wave-number range ($k > 1 \text{ \AA}^{-1}$). As shown in Fig. 1 and Fig. S2 in the Supplemental Material [95], similar to pure water, the response function retains both the main peak and the satellite shoulder, indicating minimal perturbation by the added ions. This observation suggests that the relatively low ion-concentration is insufficient to effectively disrupt the hydrogen-bonding network among water molecules, as evidenced that the number of HBs per water molecule decreases less than 5% over this concentration range (Fig. S4 in the Supplemental Material [95]). Consequently, the dielectric response function predominantly reflects the properties of the solvent, with the presence of ions exerting only a minor influence apart from near $k = 0$, observed as a slight reduction in the dielectric overscreening resonance.

At a concentration of 0.98 M, the magnitude of the primary peak in $\chi(k)$ decreases from 40.2 to 38.0, accompanied by a slight increase in the response function in the moderate wave-number region ($k < 3 \text{ \AA}^{-1}$). As the concentration further increased to 3.60 M, the changes become more visible. Although the position of the maximum peak remains almost unchanged, its amplitude diminishes to 33.9, accompanied by a new shoulder emerging at approximately $2.2 \text{ \AA}^{-1}$. This shift indicates that the dielectric over-screening effect extends to lower k values.

Essentially, analysis of pair correlations reveals that this newly formed feature at $2.2 \text{ \AA}^{-1}$ corresponds to synergistic peaks in both $\text{Na}^+ - \text{O}$ and $\text{Cl}^- - \text{O}$ correlations (Figs. S5 and S6 in the Supplemental Material [95]), indicating the growing influence of ion-solvent interactions. Concurrently, the intermolecular O-O peak at $\approx 3.0 \text{ \AA}^{-1}$ (corresponding to $2.1 \text{ \AA}$ in real space), weakens and gradually shifts toward $2.2 \text{ \AA}^{-1}$ (corresponding to a larger characteristic length, $2.9 \text{ \AA}$), indicating that the local water structure (“water-water” correlations) becomes looser owing to the presence of ions, accomplished with a disturbance of hydrogen-bonding network among water molecules (Fig. S4 in the Supplemental Material [95]). Furthermore, compared with the dilute aqueous electrolyte, the coordination number between ions gets more pronounced, indicating the formation of ionic aggregation in the

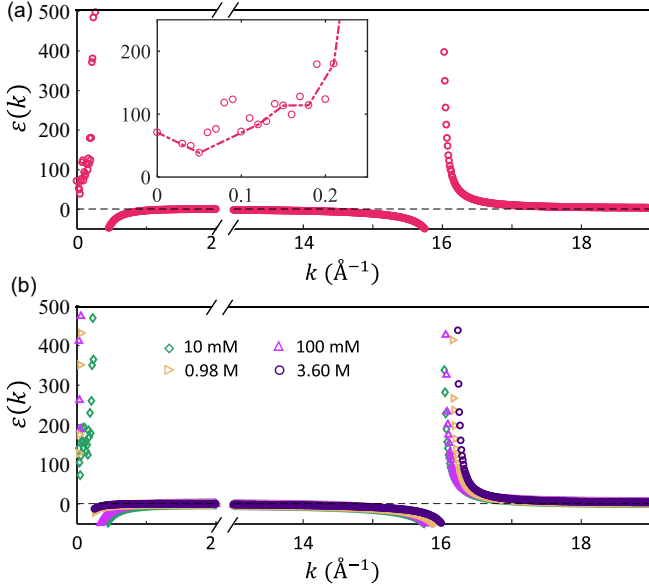


FIG. 2. Features of the nonlocal dielectric function at different electrolyte concentrations. (a) The dielectric function $\varepsilon(k)$ for pure water. Inset shows its behavior in the small wave-number domain. The macroscopic value for pure water, $\varepsilon(k=0) \approx 71.01$, has been obtained by simulation using Eq. (44). (b) The dielectric function $\varepsilon(k)$ for aqueous NaCl electrolyte of various concentrations.

high-concentration electrolytes. As we will see, at 3.6 M, we have the beginning of the formation of oscillating patterns in the ionic subsystem of the solution of a period different from that of the water structural patterns.

Although the accuracy of the simulation data at small k region is limited, we may solidly assert that the dielectric response function exhibits a clear dependence on concentration in $k < 1 \text{ \AA}^{-1}$ regime (inset of Fig. 1). Specifically, the dielectric polarization response function apparently increases with rising concentration at moderate concentrations, highlighting the significant roles of both interionic interactions and ion-water interactions in screening. The numerical accuracy of this plot is low for small k .

B. Static dielectric function

We now turn our attention to the nonlocal dielectric function, $\varepsilon(k) = \{1 - \chi(k)\}^{-1}$. As illustrated in Fig. 2(a), three well-distinguished regions are observed for pure water, aligning well with the findings of Ref. [52]. Specifically, in the “*small-k* regime,” $\varepsilon(k)$ exhibits positive values where it decreases from the macroscopic dielectric constant ε (≈ 71.0 for this model of water) at $k = 0$ to approximately 36.03 at $k \approx 0.05 \text{ \AA}^{-1}$ and then rising again, delivering a kind of Lorentzian functional behavior [20,52]. In the *intermediate-k* range, the dielectric function becomes negative, reflecting the dielectric overscreening phenomenon owing to the alternating layers in the bound charge distribution. In this range, the vectors $\mathbf{E}_k$ and the $\mathbf{D}_k$ in Eq. (6) have different signs so they point in opposite directions. Finally, in the high- k regime ($k > 16 \text{ \AA}^{-1}$), $\varepsilon(k)$ returns to positive values and decreases monotonically, asymptotically approaching the high wave-number limit ($\varepsilon(k \rightarrow \infty) = 1$). The fact that

$\varepsilon(k)$ has a divergence and jumps between $+\infty$ and $-\infty$ when it changes sign simply means that $\mathbf{E}_k = \mathbf{D}_k/\varepsilon(k)$ passes zero at the k value where $1/\varepsilon(k)$ is zero and $\chi(k)$ is equal to one.

For aqueous NaCl electrolytes [Fig. 2(b)], the dielectric function $\varepsilon(k)$ exhibits a virtually concentration-independent behavior in both the intermediate- and high- k regimes. There it retains a negative value in the intermediate- k range, transitioning to positive values and monotonically decreasing to 1 with k^{-2} way in the high- k region, reflecting solvent-dominated characteristics in these regions. The only notable change is a slight shift of the second divergence point toward higher k wavevectors, indicating subtle perturbations from ion-solvent interactions.

In contrast, the small- k regime reveals a puzzling dependence on electrolyte concentration. At low concentrations, the first divergence point of $\varepsilon(k)$ remains approximately where it is for pure water. However, at higher concentrations (e.g., beyond 0.98 M), the simulation data suggest a possible shift of the divergence point to substantially smaller k values, implying the onset of dielectric overscreening, where $\chi(k) > 1$ in the inset to Fig. 1, at surprisingly long wavelengths. This could reflect enhanced interionic and ion-solvent correlations that give rise to collective polarization modes. However, interpretation of this behavior requires caution, as pointed out earlier. The reliability of simulation-derived $\varepsilon(k)$ in this regime is potentially compromised by the artifacts that may be caused by the finite size of the simulation box and statistical uncertainties. All in all, while the observed trends are suggestive, we refrain from drawing definitive conclusions regarding the dielectric behavior at small k , and instead view this as a direction for further investigation with larger-scale simulations and complementary theoretical analyses.

C. Rationalizing the dielectric factor $\mathcal{E}^*(\kappa)$: Static macroscopic dielectric constant as a function of electrolyte concentration

In the exact expression for the leading decay parameter κ ,

$$\kappa^2 = \frac{4\pi}{k_B T \mathcal{E}^*(\kappa)} \sum_j n_j q_j q_j^*, \quad (43)$$

[Eq. (29) with $\kappa_1 = \kappa$], the dielectric factor $\mathcal{E}^*(\kappa)$ replaces the dielectric constant ε in the traditional definition, Eq. (30), of the Debye parameter κ_D . In practice, it is quite common to extend the use of the latter to higher electrolyte concentrations by using a concentration-dependent ε . Here, we will investigate the basis for this use of ε for the leading mode at low to intermediate electrolyte concentrations. Note that even if a modified value of ε is used in κ_D , it remains an approximate decay parameter once $q_j^* = q_j$ is assumed.

For pure polar fluids, ε can be rigorously computed from the distribution of dipoles—a well-established result of statistical mechanics. One can obtain it from simulations by using the formula:

$$\varepsilon = 1 + 4\pi \frac{\langle \hat{\mathbf{M}}^2 \rangle - \langle \hat{\mathbf{M}} \rangle^2}{3V k_B T}, \quad (44)$$

where $\hat{\mathbf{M}}$ is the dipole moment of the simulation box and V is its volume; $\langle \hat{\mathbf{M}} \rangle$ should and does vanish for a long simulation.

Alternatively, other exact expressions for ε exist for pure polar fluids. For example, Nienhuis and Deutch [96] give it as

$$\varepsilon = 1 + \frac{4\pi n_p}{k_B T} \cdot \frac{\boldsymbol{\mu}_p \cdot \boldsymbol{\mu}_p^*}{3}, \quad (45)$$

where n_p is the number density of polar molecules, $\boldsymbol{\mu}_p$ is the dipole moment vector for each molecule and $\boldsymbol{\mu}_p^*$ is an effective value of the latter, which includes the effects of the surrounding oriented dipoles of the other molecules. The latter entity is, in fact, the same as the dipole moment vector for the dressed particle charge-distribution $\rho_p^*(\mathbf{r})$, leading to $\boldsymbol{\mu}_p \cdot \boldsymbol{\mu}_p^* = \mu_p^2 + \boldsymbol{\mu}_p \cdot \boldsymbol{\mu}_p^{\text{dress}}$, where $\mu_p = |\boldsymbol{\mu}_p|$ and $\boldsymbol{\mu}_p^{\text{dress}}$ is the dipole moment of the dress. Inserted in Eq. (45), the term μ_p^2 in this expression gives a self-term in ε and $\boldsymbol{\mu}_p \cdot \boldsymbol{\mu}_p^{\text{dress}}$ the correlational part. Equivalent forms of Eq. (45) and the differences between some of them have been discussed by Høye and Stell. [97] In all cases, ε only contains contributions from the distribution of dipoles and a pertinent question is if something similar is true for electrolyte solutions.

It is therefore of interest to investigate the dielectric factor $\mathcal{E}^*(\kappa) = \varepsilon_{\text{reg}}(i\kappa)$ for dilute electrolyte solutions, i.e., for small κ . In the exact expression (43), the entity $\mathcal{E}^*(\kappa)$ indeed has the role of a concentration-dependent “dielectric constant” of the solution. However, let us first see what $\mathcal{E}^*(\kappa)$ is for a classical plasma of hard-sphere ions, where only ions are present (see also Ref. [49]). In this case, Eq. (19) becomes $\Lambda^*(k) = -\sum_j n_j q_j \rho_{j,k}^* / [k_B T]$ and we have from Eq. (23)

$$\mathcal{E}^*(\kappa) = \varepsilon_{\text{reg}}(i\kappa) = 1 + \frac{4\pi \sum_j n_j q_j [\rho_{j,k}^* - \rho_{j,0}^*]}{k^2 k_B T} \Big|_{k=i\kappa}. \quad (46)$$

To obtain the leading behavior for small κ , we will need to extract the k^2 term from $\rho_{j,k}^* - \rho_{j,0}^*$. Using the Fourier transform definition, one can show that this term is equal to $-k^2 m_j^{(2)} / 3!$, where $m_j^{(2)} = \int d\mathbf{r} \, r^2 \rho_j^*(r)$ is the second moment of ρ_j^* . Thus, we have

$$\mathcal{E}^*(\kappa) = 1 - \frac{\frac{4\pi}{k_B T} \sum_j n_j q_j m_j^{(2)}}{6} + O(\kappa^2), \quad (47)$$

for the plasma. The higher-order terms in κ contain higher-order moments of $\rho_j^*(r)$. It follows that in ionic systems, $\mathcal{E}^*(\kappa)$ always has a contribution from the ion-ion correlations that remains when κ is small.

As a concrete example that has important ion-ion contributions given by Eq. (47), we mention systems where the anions and cations correlate strongly with each other and form ion pairs. It is easy to show [49] from Eq. (47) that the pairs give a contribution to $\mathcal{E}^*(\kappa)$ that is equal to $4\pi n_{\text{pair}} \mu_{\text{pair}}^2 / [3k_B T]$, where n_{pair} is the number density of pairs, and μ_{pair} is the dipole moment of each pair. This contribution from the ion pairs is the same as the dipolar self-term in the dielectric constant in Eq. (45). The dipole-dipole and charge-dipole correlations are contained in the remaining contributions to $\mathcal{E}^*(\kappa)$ from $\rho_j^*(r)$. It is, however, not necessary with actual pairing for the term in Eq. (47) to be significant—it also contributes when the anion-cation correlations are strong, which occur at high concentrations.

Moreover, ion-ion correlations also give other important contributions to $\mathcal{E}^*(\kappa)$. At sufficiently high ion

concentration, another decay mode, which is a solution κ' to Eq. (43) with $\kappa' > \kappa$, merges with the leading mode, whereby both decay parameters become complex-valued (κ and κ' are then complex conjugates to each other). This is the so-called *Kirkwood crossover point* mentioned earlier, where the tails of the screened Coulomb potential and the pair correlation functions go from monotonic to oscillatory exponential decay. For low concentrations, κ' is very large (i.e., a very short decay length), so it gives a negligible contribution for most r values, but κ' decreases toward κ when the concentration is increased. Before the crossover, the value of $\mathcal{E}^*(\kappa)$ is affected very strongly by the ion-ion correlations, and at this point κ and $\mathcal{E}^*(\kappa)$ become complex-valued.

Returning to dilute electrolyte solutions with molecular solvent, the function $\varepsilon_{\text{reg}}(k)$ can be expanded in a MacLaurin series [49] $\varepsilon_{\text{reg}}(k) = b_0^* + b_2^* k^2 + \dots$, where

$$b_0^* = 1 + \frac{4\pi}{k_B T} \sum_j n_j \left[\frac{\boldsymbol{\mu}_j \cdot \boldsymbol{\mu}_j^*}{3} - \frac{1}{6} (q_j m_j^{*(2)} + q_j^* m_j^{*(2)}) \right] \quad (48)$$

and $m_j^{(2)}$ is the second moment of the j particle’s internal charge distribution ρ_j^{int} . The latter is zero for spherical ions with a central charge. We recognize the first term in the square brackets from the case of polar fluids and the second from the classical plasmas. Here, both terms contribute to $\varepsilon_{\text{reg}}(k)$ for $k = 0$. The coefficients b_m^* , $m \geq 2$, contain quadrupolar and other higher-order contributions; see Ref. [49] for explicit expressions.

It follows that in dilute electrolyte solutions we have $\mathcal{E}^*(\kappa) \approx \varepsilon_{\text{reg}}(0) = b_0^*$. In the systems that we study here, the particles that have dipole moments are uncharged, so that for small κ we have

$$\mathcal{E}^*(\kappa) \approx 1 + \frac{4\pi}{k_B T} \left[\frac{n_{\text{H}_2\text{O}} \boldsymbol{\mu}_{\text{H}_2\text{O}} \cdot \boldsymbol{\mu}_{\text{H}_2\text{O}}^*}{3} - \frac{n_{\text{salt}} e (m_{\text{Na}}^{*(2)} - m_{\text{Cl}}^{*(2)})}{6} \right], \quad (49)$$

where e is the unit charge. Thus, $\mathcal{E}^*(\kappa)$ contains dipolar contributions (the first term in the parentheses) as well as ionic ones (the last term). The latter includes contributions from ion-ion correlations, which, as we have seen, are present even in the absence of molecular water. Thus, the appropriate concentration-dependent “dielectric constant” *cannot be generally calculated from the dipolar contributions alone*, but as we will see, it can be a good approximation to do so in sufficiently dilute solutions.

The presence of ions affects the value of $\boldsymbol{\mu}_{\text{H}_2\text{O}}^*$ compared to that of pure water and the presence of water around the ions affects the values of $m_{\text{Na}}^{*(2)}$ and $m_{\text{Cl}}^{*(2)}$. Since $n_{\text{H}_2\text{O}} \gg n_{\text{salt}}$ in dilute solutions, the dipolar term dominates in $\mathcal{E}^*(\kappa)$ and it can be a good approximation to evaluate the “dielectric constant” solely from the distribution of dipoles. This is commonly done in the literature, but one must keep in mind that this is an approximation and that the ionic terms matter at higher concentrations. Furthermore, when κ is not small we have $\mathcal{E}^*(\kappa) = \varepsilon_{\text{reg}}(i\kappa) = b_0^* - b_2^* \kappa^2 + \dots$, so the quadrupolar and higher-order contributions cannot be neglected.

Note that $\mathcal{E}^{\text{eff}}(\kappa)$ in Eq. (27) also has the role of a kind of concentration-dependent “dielectric constant” of the solution. While $\mathcal{E}^*(\kappa) \approx \mathcal{E}^{\text{eff}}(\kappa)$ in dilute solutions, they are not equal at higher concentrations because $\mathcal{E}^{\text{eff}}(\kappa) = b_0^* - 2b_2^*\kappa^2 + \dots$ as follows from its definition and the expansion of $\varepsilon_{\text{reg}}(k)$.

When the concentration is low, we can accordingly use the approximation $b_0^* \approx \varepsilon_{\text{dip}}(c)$, where $\varepsilon_{\text{dip}}(c)$ is the concentration-dependent dielectric constant evaluated from the dipole-dipole correlations alone (but affected by the presence of electrolyte), for example, via Eq. (44), and c is the salt concentration. Hence, $\mathcal{E}^*(\kappa) \approx \varepsilon_{\text{dip}}(c)$ and $\mathcal{E}^{\text{eff}}(\kappa) \approx \varepsilon_{\text{dip}}(c)$ will be reasonable approximations and it follows that the screened Coulomb potential in Eq. (27) decays in dilute solutions like

$$\varphi^*(r) \sim \frac{e^{-\kappa r}}{\mathcal{E}^{\text{eff}}(\kappa) r} \approx \frac{e^{-\kappa r}}{\varepsilon_{\text{dip}}(c) r} \quad (50)$$

and, likewise, in the decay of the leading term for the pair correlation function, Eq. (33), $\mathcal{E}^{\text{eff}}(\kappa)$ can be approximated by $\varepsilon_{\text{dip}}(c)$. In the following sections we will investigate for what concentrations the approximation $b_0^* \approx \varepsilon_{\text{dip}}(c)$ is reasonable for monovalent electrolyte solutions in water.

For moderately large and high concentrations of monovalent ions, $\mathcal{E}^*(\kappa)$ and $\mathcal{E}^{\text{eff}}(\kappa)$ change character because the ion-ion correlation contributions are essential. For multivalent ions, such correlations are also important in rather dilute solutions.

Note that the approximation $\mathcal{E}^*(\kappa) \approx \varepsilon_{\text{dip}}(c)$ only applies to the leading decay mode $\kappa = \kappa_1$ when κ is small. Recall that for the other modes with decay parameters κ_ν with $\nu \geq 2$, the dielectric factor $\mathcal{E}^*(\kappa_\nu)$ in Eq. (29) has completely different values. For pure polar fluids, we have seen that $\varepsilon(i\kappa_\nu) = 0$ is equivalent to $\mathcal{E}^*(\kappa_\nu) = 0$ when $\nu \geq 2$, so the dielectric factor is zero for the higher decay modes [98].

D. Pair correlation functions, low concentrations

In this and the following sections, we will consider the ion-ion correlation functions for the aqueous electrolytes, focusing on $h_{\text{IJ}}^{\text{ions}}(r)$ for IJ = QQ, NN and NQ defined in Eq. (39). The Yukawa function terms in Eq. (42) give

$$rh_{\text{IJ}}^{\text{ions}}(r) = C_{\text{IJ}}e^{-\kappa_1 r} + D_{\text{IJ}}e^{-\kappa_2^{\text{Im}} r} \cos(\kappa_2^{\text{Im}} r + \vartheta_{\text{IJ}}(\kappa_2)) + \dots, \quad (51)$$

with coefficients $C_{\text{IJ}} = -q_{\text{I}}^{\text{eff}}(\kappa_1)q_{\text{J}}^{\text{eff}}(\kappa_1)/[k_{\text{B}}T\mathcal{E}^{\text{eff}}(\kappa_1)]$ and D_{IJ} given in Eq. (42).

Figure 3(a) shows the absolute value of $rh_{\text{QQ}}^{\text{ions}}(r)$ on a semilogarithmic scale for dilute solutions (10–500 mM). It is demonstrated that the leading term of $h_{\text{QQ}}^{\text{ions}}(r)$, which is a Yukawa function, appears as a straight line. In the large r tail, the curves exhibit a linear behavior with a decay length $1/\kappa_1$ until it is overcome by simulation noise, where the function is very small. For smaller r , oscillatory features emerge with a wavelength of ≈ 0.20 nm, reflecting the hydration shell structuring around the ions.

To quantify the screening behavior, the leading decay parameter $\kappa = \kappa_1$ can be determined by fitting a line to the straight part of each curve [colored lines in the Fig. 3(a)]. The corresponding decay length $\lambda = 1/\kappa$ (reported as λ_{fit} in

TABLE I. Concentration-dependent dielectric constant $\varepsilon = \varepsilon_{\text{dip}}(c)$ obtained from simulations by use of Eq. (44), the Debye length λ_D calculated using that ε , and the simulated decay length, $\lambda_{\text{fit}} = 1/\kappa$, obtained from the fit of $|rh_{\text{QQ}}(r)| \sim \exp(-\kappa r)$ to the data in Fig. 3(a). The estimated $\lambda = 1/\kappa$ for 0.98 and 1.9 M (not shown) obtained from Fig. 4 are approximately equal to λ_D .

Concentration (M)	ε	λ_D (nm)	λ_{fit} (nm)
0.010	71.31	2.91	2.6
0.050	70.69	1.29	1.29
0.10	69.45	0.91	0.92
0.50	63.72	0.39	0.38
0.98	59.87	0.27	
1.90	52.21	0.18	
3.60	43.61	0.12	

Table I) is plotted in Fig. 3(b) as a function of concentration. It is compared to the Debye length $\lambda_D = 1/\kappa_D$, which has been calculated using a concentration-dependent dielectric constant $\varepsilon_{\text{dip}}(c)$ evaluated by simulation from the dipole distributions alone [Eq. (44)]. The close agreement between λ_{fit} and λ_D shows that the approximation $\kappa \approx \kappa_D$ is valid in this concentration regime. Minor deviations at 10 mM are likely due to the statistical limitations, as only 60 ions are present in the simulation box for this concentration.

To further interpret the contributions from the distinct ionic correlations, taking 50 mM as an example, Fig. 3(c) presents the functions $rh_{\text{IJ}}^{\text{ions}}(r)$ for IJ = QQ, NN and NQ. Among these, the charge-charge correlation $h_{\text{QQ}}^{\text{ions}}(r)$ clearly dominates over the other two functions, which are much smaller in the tail region and are soon overcome by simulation noise when r is increased. The small magnitude of $h_{\text{NN}}^{\text{ions}}(r)$ reflects the near-equality of $g_{++}(r)$ and $g_{--}(r)$, particularly in the tail region, so we have $[q_+^{\text{eff}}(\kappa_1)]^2 \approx [q_-^{\text{eff}}(\kappa_1)]^2$. This implies that the effective charges of opposite signs have nearly the same absolute values, $q_+^{\text{eff}}(\kappa_1) \approx -q_-^{\text{eff}}(\kappa_1)$. In the case of $h_{\text{NN}}^{\text{ions}}(r)$, the oscillatory mode can be seen in the range shown—until the noise take over. The oscillations are superimposed on a monotonic contribution with a short decay length different from λ . Although all correlation functions are expected to have the same decay length for sufficiently large r , the coefficient for the κ_1 term in $h_{\text{NN}}^{\text{ions}}(r)$, which contains the factor $[q_{\text{NN}}^{\text{eff}}(\kappa_1)]^2$, is very small, and this contribution cannot be seen due to the noise. Note that $q_+^{\text{eff}}(\kappa_1) \approx -q_-^{\text{eff}}(\kappa_1)$ implies that

$$q_{\text{N}}^{\text{eff}}(\kappa_1) = [q_+^{\text{eff}}(\kappa_1) + q_-^{\text{eff}}(\kappa_1)]/2 \approx 0, \quad (52)$$

while $q_{\text{Q}}^{\text{eff}}(\kappa_1)$ is large since it is equal to $[q_+^{\text{eff}}(\kappa_1) - q_-^{\text{eff}}(\kappa_1)]/2$. Consequently, $h_{\text{QQ}}^{\text{ions}}(r)$ has a much larger tail in agreement with the figure.

The origin of the oscillatory behavior in $h_{\text{QQ}}^{\text{ions}}$ and $h_{\text{NN}}^{\text{ions}}$ is clarified in Fig. 3(d). As defined in Eq. (39), both functions contain the contribution $[h_{++}(r) + h_{--}(r)]/4$, while differing only in the sign of $h_{+-}(r)/2$ term. The oscillations in $g_{++}(r)$ and $g_{--}(r)$ are nearly out-of-phase, resulting in partial cancellation in the sum. Therefore, the dominant source of the

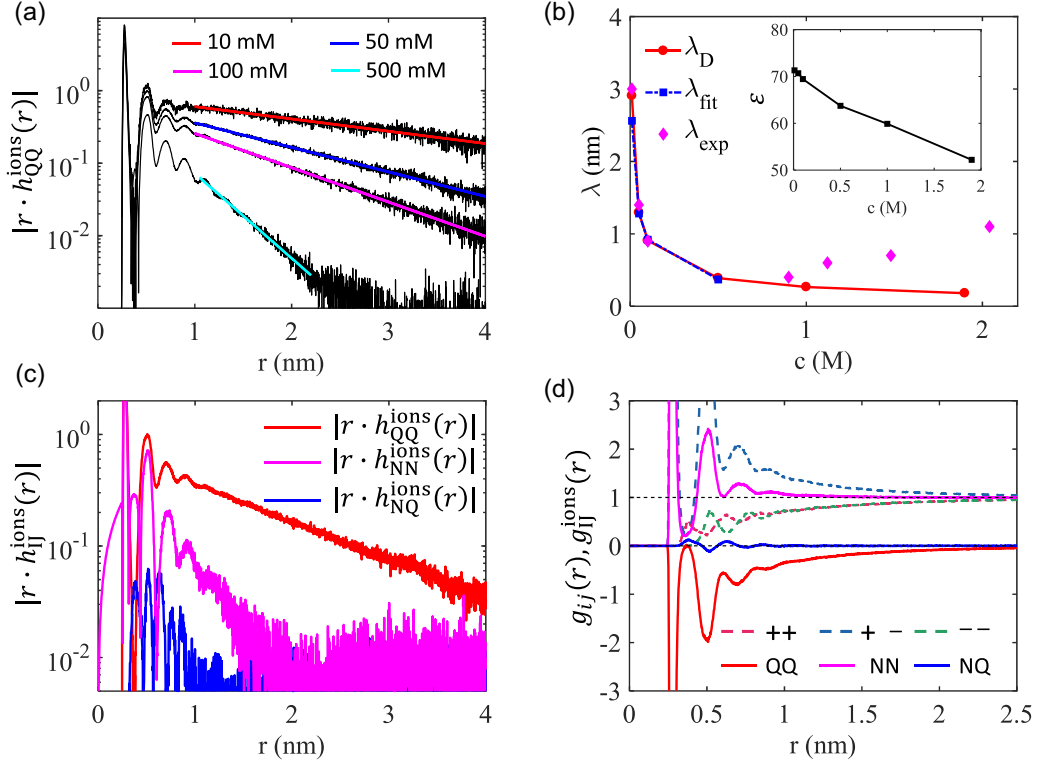


FIG. 3. Ionic distribution functions for aqueous NaCl solutions. (a) Semilogarithmic plot of $|r \cdot h_{QQ}^{\text{ions}}(r)|$ as a function of r for various electrolyte concentrations. The black curves are the original data. The red, blue, pink, and cyan straight lines represent fits of $|r \cdot h_{QQ}^{\text{ions}}(r)| \sim \exp(-\kappa r)$ for 10, 50, 100, and 500 mM electrolyte concentrations, respectively. (b) The dependence on the electrolyte concentration c of the Debye length $\lambda_D = 1/\kappa_D$ (red points and line)—calculated with a concentration-dependent dielectric constant $\varepsilon = \varepsilon_{\text{dip}}(c)$ of water as obtained from the simulation via Eq. (44). The screening length $\lambda = 1/\kappa$ (blue points and line) is extracted from the data shown in panel (a). The estimated λ for 0.98 and 1.9 M obtained from Fig. 4 are approximately equal to the plotted λ_D . Experimental decay lengths from surface force measurements between mica surfaces [14] are shown as pink diamonds. The inset shows the concentration-dependent $\varepsilon_{\text{dip}}(c)$ for various aqueous electrolytes obtained from Eq. (44). The character of that curve is in line with established experimental data [99,100]. (c) $|r \cdot h_{IJ}^{\text{ions}}(r)|$ for $IJ = QQ, NN$ and NQ [defined in Eq. (39)] as a function of r for a 50 mM solution. (d) $g_{ij}(r)$ and $g_{ij}^{\text{ions}}(r)$ plotted as functions of r for 50 mM. The latter functions are defined in analogy to h_{ij}^{ions} in Eq. (39), whereby $g_{NN}^{\text{ions}} = h_{NN}^{\text{ions}} + 1$ and $g_{IJ}^{\text{ions}} = h_{IJ}^{\text{ions}}$ for the rest.

observed oscillations in both $h_{QQ}^{\text{ions}}(r)$ and $h_{NN}^{\text{ions}}(r)$ is primarily the $h_{+-}(r)/2$ contribution. Interesting, the structure of $h_{+-}(r)$ provides insight into the solvent-mediated arrangement of ions. The first maxima, located just beyond the anion-cation contact distance, corresponds to a configuration in which a water molecule separates the cation and anion. Notably, differences in cation-cation and anion-anion distributions further highlight distinct hydration environments.

E. Pair correlation functions, higher concentrations

What is the screening behavior at higher concentration? The extraction of screening behavior becomes more challenging due to increased noise in the long-range tail of $r h_{QQ}^{\text{ions}}(r)$. This function is plotted in Fig. 4(a) for the concentrations 0.5, 1.0 and 1.9 M. Despite the noise, the monotonic exponential decay, corresponding to the first term in Eq. (51), remains discernible, and it is still possible to extract the oscillatory part in the second term. To facilitate this, we adopt the approximation $\kappa \approx \kappa_D$ as calculated with the concentration-dependent dielectric constant $\varepsilon_{\text{dip}}(c)$ given in Table I. The first term of Eq. (51), $C_{QQ} e^{-\kappa_D r}$, with a fitted value of the prefactor is plotted in the figure as dashed curves. The fitting is

done so that the function $r \Delta h_{QQ}^{\text{ions}}(r) \equiv r h_{QQ}^{\text{ions}}(r) - C_{QQ} e^{-\kappa_D r}$ decays like $D e^{-a r} \cos(b r + \vartheta)$ for some D , a , b , and ϑ for large r , that is, like the second, oscillatory term in Eq. (51).

Figure 4(b) shows the resulting $r \Delta h_{QQ}^{\text{ions}}(r)$. For $r \gtrsim 0.7$ nm, a clear oscillation is observed with a wavelength of 0.20 nm, consistent with the structural periodicity seen for lower concentrations. For smaller r , there are other contributions that matter too, so $r \Delta h_{QQ}^{\text{ions}}(r)$ deviates from the simple oscillatory form. The insert shows the fit of $D e^{-a r} \cos(b r + \vartheta)$ to the function $r \Delta h_{QQ}^{\text{ions}}(r)$ for the case 1.0 M. The fit is very good for $r \gtrsim 0.55$ nm in the range shown. The fits for the other concentrations in Fig. 4(b) (not shown) are about equally good for $r \gtrsim 0.55$ nm (0.5 M) and for $r \gtrsim 0.70$ nm (1.9 M). In all three cases, the decay length $1/a = 1/\kappa_2^{\text{Re}} = 0.22$ nm and the wavelength $2\pi/b = 2\pi/\kappa_2^{\text{Im}} = 0.20$ nm, so both are independent of the ion concentration, while the magnitude and phase vary a little. Thus, we see that the second term in Eq. (51) describes $r \Delta h_{QQ}^{\text{ions}}(r)$ very well apart from small r .

The success in these fittings shows that we indeed have $\kappa \approx \kappa_D$ within the accuracy of the simulation for concentrations up to at least 1.9 M NaCl in aqueous

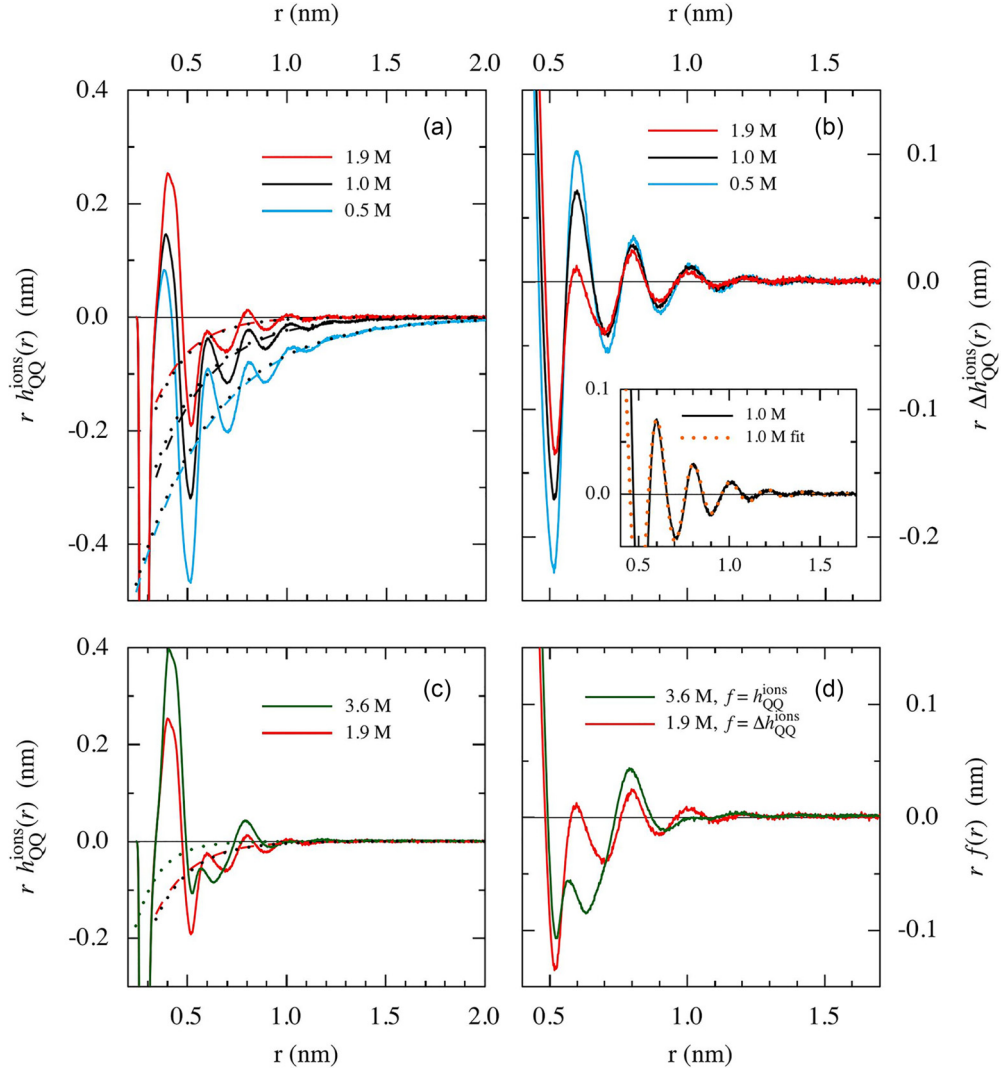


FIG. 4. (a) The ionic charge-charge correlation function h_{QQ}^{ions} as a function of r for 0.5, 1.0 and 1.9 M aqueous NaCl solutions [for 0.5 M it is the same as in Fig. 3(a)]. The full curves show $rh_{QQ}^{\text{ions}}(r)$, while the dashed curves show $C_{QQ}e^{-\kappa_1 r}$, that is, the first term in Eq. (51), which dominates for large r . The dotted curves show the latter when the pre-factor is approximated as $C_{QQ} \approx C_0 = -e^2/[k_B T \varepsilon_{\text{dip}}(c)]$. (b) The remainder $r\Delta h_{QQ}^{\text{ions}}(r) \equiv rh_{QQ}^{\text{ions}}(r) - C_{QQ}e^{-\kappa_1 r}$, where the first term is subtracted. It is dominated for large r by the second term in Eq. (51). The insert shows an example of a fit of the second term in Eq. (51) to $r\Delta h_{QQ}^{\text{ions}}(r)$. The full line shows the same curve as in the main frame (b) for 1 M solution and the dotted line shows the corresponding fitted curve. (c) The same as frame (a), but for the concentrations 1.9 and 3.6 M. (d) A comparison between the function $rh_{QQ}^{\text{ions}}(r)$ for the 3.6 M solution and $r\Delta h_{QQ}^{\text{ions}}(r)$ for 1.9 M.

solution. The dotted curves in Fig. 4(a) show $C_0 e^{-\kappa_D r}$ with $C_0 = -e^2/[k_B T \varepsilon_{\text{dip}}(c)]$, that is, if $q_Q^{\text{eff}}(\kappa_1)$ is equal to the bare ionic charge e and $\mathcal{E}^{\text{eff}}(\kappa_1) = \varepsilon_{\text{dip}}(c)$. We see that these curves are close to the solid ones, which indicates that the values of κ , $q_Q^{\text{eff}}(\kappa_1)$, and $\mathcal{E}^{\text{eff}}(\kappa_1)$ are nearly the same as in the absence of ion-ion correlations. These conclusions apply, in fact, also to the lower concentrations shown in Fig. 3, but since $q_i^{\text{eff}}(\kappa_1) \rightarrow q_i$ and $\mathcal{E}^{\text{eff}}(\kappa_1) \rightarrow \varepsilon$ when the concentration goes to zero, this is to be expected.

However, the lack of influence of the ion-ion correlations on κ and $q_Q^{\text{eff}}(\kappa_1)$ up to at least 1.9 M is only apparent and depends most likely on the counteracting influence of two effects. Let us compare to the situation for aqueous electrolyte solutions in the primitive model (in which the solvent is

modelled as a dielectric continuum), where the ion-ion correlations are very important at these concentrations. In the restricted primitive model, where all ions have the same size, the electrostatic coupling strength can be measured by the dimensionless quantity $\beta_R = q^2/(\varepsilon k_B T d)$, where d denotes the ionic diameter. For $\beta_R \lesssim 2.5$, which corresponds to monovalent ions when $\varepsilon \approx 80$, it has been found that $\kappa > \kappa_D$ and $|q_i^{\text{eff}}| > q$, and when β_R is about 6 to 10, corresponding to divalent ions, $\kappa < \kappa_D$ and $|q_i^{\text{eff}}| < q$ [23,36,101]. However, in the present case, the calculated $\varepsilon_{\text{dip}}(c)$ is appreciably smaller than 80 and β_R lies in the range around 3 to 4 for concentrations between 0.1 and 2 M when $d \approx 0.27$ nm, as estimated from the simulated $g_{+-}(r)$. For these β_R values, $\kappa \approx \kappa_D$ and $|q_i^{\text{eff}}| \approx q$ within about 5% margin also in the primitive model for the

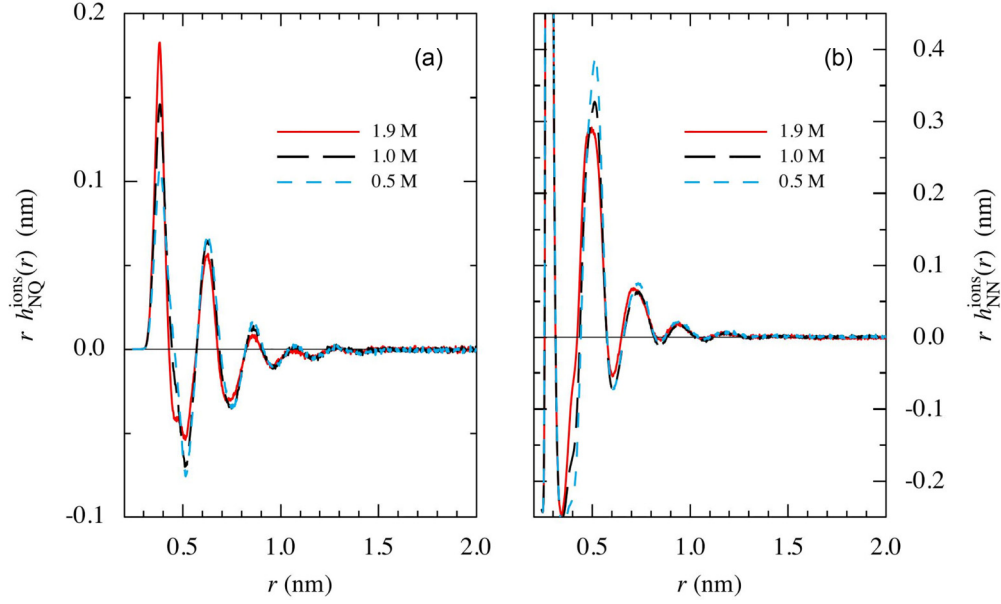


FIG. 5. (a) The ionic density-charge correlation function $h_{NQ}^{\text{ions}}(r)$ as a function of r for 0.5, 1.0 and 1.9 M aqueous NaCl solutions plotted as $r h_{NQ}^{\text{ions}}(r)$. (b) The corresponding density-density correlation function $r h_{NN}^{\text{ions}}(r)$ as a function of r for the same systems.

concentrations in question. Thereby, the steric ion-ion correlations, which dominate for small β_R , and the electrostatic ones, which dominate for large β_R , counteract each other. This means that the two different aspects of the correlations happen to have a small net effect at the present conditions.

To further probe the concentration dependence of screening, we analyze the behaviors of $h_{NQ}^{\text{ions}}(r)$ and $h_{NN}^{\text{ions}}(r)$. Across the range 0.5 to 1.9 M, $h_{NQ}^{\text{ions}}(r)$ remains remarkably similar for $r \gtrsim 0.5$ nm as shown in Fig. 5(a). In fact, $h_{NQ}^{\text{ions}}(r)$ for 50 mM [Figs. 3(c) and 3(d)] is nearly the same as the curves in Fig. 5(a), so $h_{++}(r) - h_{--}(r)$ for $r \gtrsim 0.5$ nm varies very little with electrolyte concentration over a wide range. This implies that the leading term of $h_{++}(r)$, which contains $[q_+^{\text{eff}}(\kappa_1)]^2$ in the coefficient, and the corresponding term in $h_{--}(r)$ nearly cancel each other, so also at these higher concentrations we have $[q_+^{\text{eff}}(\kappa_1)]^2 \approx [q_-^{\text{eff}}(\kappa_1)]^2$. Again, $q_N^{\text{eff}}(\kappa_1)$ is small, see Eq. (52), while $q_Q^{\text{eff}}(\kappa_1)$ is large, so $h_{NQ}^{\text{ions}}(r)$ has the large contribution with decay length $1/\kappa_1$ that we saw in Fig. 4(a). Since the results in Figs. 4(a) and 4(b) indicate that $q_Q^{\text{eff}}(\kappa_1) \approx q_+ = -q_-$ we can see that $q_i^{\text{eff}}(\kappa_1) \approx q_i$ up to at least 2M. The oscillations of $h_{NQ}^{\text{ions}}(r)$ have a wavelength of ≈ 0.2 nm, i.e., about the same as that of $\Delta h_{NQ}^{\text{ions}}(r)$ in Fig. 4(b).

The function $h_{NN}^{\text{ions}}(r)$ is plotted for the same three concentrations in Fig. 5(b) and since the first term in Eq. (51) contains the factor $[q_N^{\text{eff}}(\kappa_1)]^2$ in the coefficient C_{NN} , the tail with decay length $1/\kappa_1$ is small here too and cannot be seen in the plot. We see that $h_{NN}^{\text{ions}}(r)$ for $r \gtrsim 0.5$ nm varies very little with electrolyte concentration between 0.5 and 1.9 M. The wavelength is about the same as for $h_{NQ}^{\text{ions}}(r)$. In Fig. 3(c) for the 50 mM solution, we saw an oscillatory contribution in $h_{NN}^{\text{ions}}(r)$ superimposed on a monotonic decay with considerably shorter decay length than $1/\kappa_1$. A similar monotonic decay may be present at these higher concentrations, but it cannot be detected in the simulations, probably because its magnitude is too small.

We can conclude that both $h_{NN}^{\text{ions}}(r)$ and $h_{NQ}^{\text{ions}}(r)$ in Fig. 5 are dominated by solvation structure effects, while $h_{QQ}^{\text{ions}}(r)$ in Fig. 4(a) contains the typical Debye-type screening term in addition to the solvation effects up to at least 2 M solutions. The oscillatory contribution due to the solvent has about the same wavelength for $r \gtrsim 0.5$ nm in all cases, including low concentrations.

In the oscillatory patterns shown in Figs. 4(a), 4(b), and 5, the positions of the peaks exhibit only a weak dependence on electrolyte concentration. Only the first peak in Figs. 4(a) and 4(b) shows a slight shift with concentration, while the subsequent ones remain essentially unchanged. *This indicates that ions in aqueous solutions up to quite high concentrations do not generate distinct structural patterns of their own, but instead occupy the sites defined by the underlying structure of water.* The amplitude of the first peak increases with concentration, while the remaining oscillation amplitudes decreases a little. This suggests that the local structure around each ion becomes more rigid; however, this trend does not override the dominant influence of water, and up to 1.9 M no new structural motifs emerge in our data. This finding is consistent with Ref. [30], which reached a similar result for dilute solutions, and with the absence of concentration dependence in the main peak of the response function $\chi(k)$ reported in Ref. [78].

Interestingly, this behavior can be compared to predictions from primitive models of monovalent electrolytes with $d \approx 0.27$ nm for conditions that correspond to ours, where a Kirkwood transition appears above about 2 M as estimated from the data in Refs. [36,88,101]. Oscillations do not occur before then. Our observations in Figs. 4(a), 4(b), and 5 thus reinforce the view that the structure of electrolytes is fundamentally governed by the structure of water up to at least 1.9 M.

To probe the onset of structural crossover at higher concentrations, we have also simulated the case of 3.6 M. Figure 4(c) shows $r h_{QQ}^{\text{ions}}(r)$ for this case together with the corresponding

curve for 1.9 M, which is also plotted in Fig. 4(a). Unlike our findings for the lower concentrations, the function $rh_{\text{QQ}}^{\text{ions}}(r)$ for 3.6 M does not exhibit an exponential tail in the r interval shown (the simulation noise takes over at about $r \approx 1.3\text{--}1.5$ nm for 3.6 M). Although the theoretical curve $C_0 e^{-\kappa_D r}$ is plotted for 3.6 M (green dotted curve), the fitting procedure for the monotonic term described above fails to reproduce the data for any value of the prefactor C_{QQ} in Eq. (51). In Fig. 4(d), $rh_{\text{QQ}}^{\text{ions}}(r)$ for 3.6 M is compared to $r\Delta h_{\text{QQ}}^{\text{ions}}(r)$ for 1.9 M and we see that they are quite different from each other.

Within the simulation accuracy, there is no sign of any monotonic exponential tail in $rh_{\text{QQ}}^{\text{ions}}(r)$ for 3.6 M and the curve is apparently a superposition of some oscillatory contributions. These observations agree with the results for 4.43 M NaCl in SPC/E water by Zeman, Kondrat, and Holm [29], who used a very large simulation box and obtained reliable results up to $r \lesssim 2$ nm. Considering that there is clearly monotonic exponential screening in the tail up to at least 1.9 M, it is likely that 3.6 M concentration lies above a Kirkwood crossover point, where the monotonic screening becomes replaced by an oscillatory one. However, due to the lack of simulation accuracy, one cannot reliably make a fit to the oscillatory contributions in the tail region.

It is also of interest to compare with other aqueous electrolytes. Coles *et al.* [28] have done simulations for the $h_{ij}(r)$ and $h_{\text{ij}}^{\text{ions}}(r)$ correlation functions for other salt solutions in SPC/E water, but for smaller simulation boxes (up to about half the linear size compared to ours). Their results are qualitatively like ours. For LiCl solutions with concentrations less than 1 M, the decay length in the tails agrees with the Debye length calculated with a concentration-dependent dielectric constant. In the other cases that they had investigated, for example, NaI, the concentration must be lower for this to be true.

The question about the existence of a monotonically decaying exponential tail in the interactions is an important issue because long-range monotonic tails have been found for surface interaction measurements in ionic fluids and electrolyte solutions; for a recent review see Ref. [35]. It is a statistical mechanical fact that the decay of surface forces between two bodies at large separations has the same decay length as the bulk electrolyte in contact with the bodies. There may be surface force contributions that are induced by the interactions between the electrolyte and the surfaces, but only those that are commensurate with the decay modes of the bulk survive for large separations. Possible reasons for a long decay length $1/\kappa_v$ of a mode can be (i) small values of the dressed ionic charges q_j^* and/or (ii) large values of $\mathcal{E}^*(\kappa_v)$ in Eq. (29) (cf. Sec. VI B of Ref. [50], where various theoretical possibilities for such a long-range mode have been investigated).

The experimentally observed decay length for aqueous NaCl solutions is considerably longer than the Debye length when the concentration is above about 1 M. For example, for 2 M solution, the measured force curve is oscillatory up to a surface separation of about 3 nm, whereafter a long-range monotonic decay is seen with decay length 1.1 nm. For a 4 M solution, the monotonic decay length is 2.2 nm [14]. The experimental values of the decay length up to about 2 M are shown as symbols in Fig. 3(b). As we

concluded earlier, for a 1.9 M solution $\lambda \approx \lambda_D = 0.18$ nm in our simulations, that is, a factor of about 6 smaller than the measured one. Thus, at least up to this concentration, the ionic charge-charge correlation $h_{\text{QQ}}^{\text{ions}}(r)$ has a Debye-type plain exponential mode with a decay length $1/\kappa$ approximately equal to the Debye length calculated with $\varepsilon_{\text{dip}}(c)$ and a magnitude near the value $C_0 = -e^2/[k_B T \varepsilon_{\text{dip}}(c)]$, which is based on the assumption that all ions have effective charges equal to their bare charges. These results indicate that $q_j^* \approx q_j$ and $\mathcal{E}^*(\kappa) \approx \varepsilon_{\text{dip}}(c)$; the latter is reduced compared to ε for pure water. Therefore, we can rule out the possibility that the much larger decay length observed experimentally at the same concentrations arises in the simulated system as a Debye-type mode with a large decay length. Such a mode would have required a significant depletion of free ions—due to ion pairing or similar associations—leading to a substantial reduction in the values of the dressed ionic charges q_j^* and the effective charges $q_j^{\text{eff}}(\kappa)$ compared to the bare value q_j .

We can, in fact, make an even stronger conclusion. An important result of the DIT analysis [50,51] of realistic systems is that any Yukawa function contribution to the free energy of interparticle interactions (or plain exponential contribution between two planar walls) must have a decay parameter κ_v that satisfies $\varepsilon(i\kappa_v) = 0$ and hence also Eq. (29). We have concluded that $q_j^* \approx q_j$ and we will now investigate $\mathcal{E}^*(\kappa_v)$ in the denominator of the latter equation. As we found earlier, $\mathcal{E}^*(\kappa) \approx \varepsilon_{\text{dip}}(c) \approx \varepsilon_{\text{reg}}(0) = \mathcal{E}^*(0)$, so $\mathcal{E}^*(\kappa)$ and $\mathcal{E}^*(0)$ are nearly equal. Recall that for any κ' we have the expansion $\mathcal{E}^*(\kappa') = b_0^* - b_2^* \kappa'^2 + \dots = \mathcal{E}^*(0) - b_2^* \kappa'^2 + \dots$. A decay length that is much larger than $1/\kappa$, that is, a decay parameter κ' in the interval $0 < \kappa' \ll \kappa$, is not possible because $\mathcal{E}^*(\kappa')$ cannot be very large in this interval; the κ'^2 and the higher-order terms in the expansion are apparently negligible there. This implies that a decay mode with a very long decay length ($\kappa' = \kappa_v \approx 0$) cannot be obtained as a solution of Eq. (29) for the simulated system, at least for concentrations up to about 1.9 M.

It is illuminating to compare with model systems where very long-ranged correlations do occur. In simulations of classical plasmas and bulk electrolytes in the primitive model, monotonic long-range charge-charge correlations appear at high electrostatic coupling (i.e., high ionic valencies, low ε , and/or low temperatures) for low to intermediate densities [36]. For low electrostatic coupling, the decay length λ of the Debye-type mode is nearly equal to the Debye length, but it becomes much larger than λ_D when the coupling is increased and the ions form ion pairs and multi-ion clusters. Such clustering reduces the value of q_j^* . The magnitude of the tail with large λ is, however, always much smaller than the amplitude of the oscillatory correlations that dominate at short distances [102,103]. This is a general feature of long-range charge-charge correlations in electrolytes because their magnitude is inversely proportional to λ^4 [51]. Therefore, these tails may not be observed in simulations due to simulation noise.

For the present case of aqueous NaCl solutions, we can conclude that the monotonic long-range tails seen in the experiments cannot be obtained, at least not for the force field used in the present simulations.

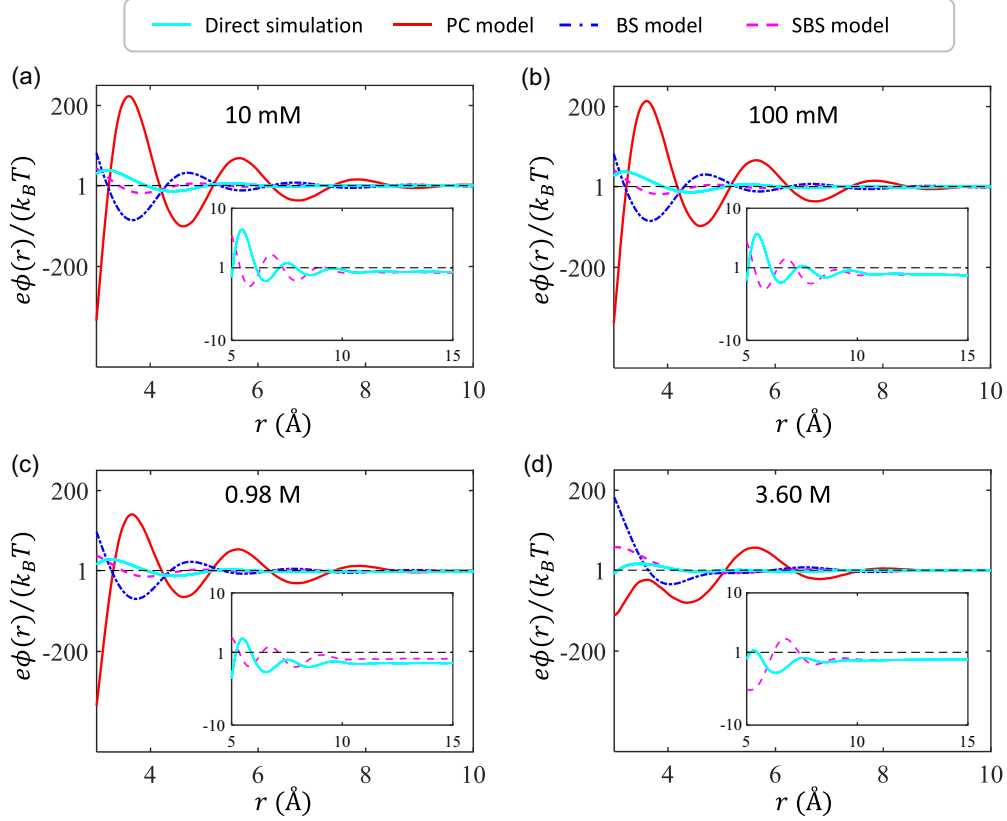


FIG. 6. Electrostatic potential created by spherically symmetric distribution of a singly charged particle in the medium with dielectric function $\varepsilon(k)$ simulated in this study. The electrostatic potential is presented in the unit of thermal voltage $k_B T/e$ (25.6 mV at room temperature). The cyan solid line is the result the direct MD simulations of electrostatic potential $\phi_{\text{Na}}(r)$ from a Na^+ ion. The red-solid, blue- and pink-dashed lines were generated via the substitution of the MD simulation data for $\varepsilon(k)$ into the linear response formula, Eq. (53), assuming the PC, BS, and SBS models for $\rho^{\text{ext}}(r)$. For the Born sphere model, the ion radius was taken as 1.47 Å. For Smeared Born Sphere model, the parameters were used as: $a = 1.47$ Å; $\eta = 0.5$ Å. The black dashed line marks the reference level $e\phi(r)/(k_B T) = 1$. The insets in all panels show the correspondence between the SBS linear response calculation and direct simulation.

F. Screened electrostatic potential from various charge distribution models: Is linear response approximation sufficient?

A central question in dielectric response theory is: what are the defining characteristics of the screened electrostatic potential in electrolyte systems? To address this, we analyze the potential due to a model “test ion”, nailed down in the origin of coordinate system, $\mathbf{r} = 0$. We will explore three things: (i) examine how the spatial dispersion of the dielectric function of the solution affects the electrostatic potential of the field caused by such a species, (ii) assess how its internal structure will affect such potential distribution, and (iii) compare the results with the direct MD simulation.

For a spherically symmetric test-charge distribution $\rho^{\text{ext}}(r)$, the corresponding potential is given by

$$\phi(r) = \frac{2}{\pi} \int_0^\infty \frac{dk}{\varepsilon(k)} \frac{\sin(kr)}{kr} \rho_k^{\text{ext}}, \quad (53)$$

where ρ_k^{ext} is the Fourier transform of $\rho^{\text{ext}}(r)$. This equation is equivalent to Eq. (12) that involves the screened Coulomb potential $\varphi^*(r)$ and has $\rho^{\text{ext}}(r)$ as the source of $\phi(r)$. For a point charge q at the origin, $\rho^{\text{ext}}(r) = q\delta(r)$, $\rho_k^{\text{ext}} = q$ and we recover Eq. (9) and $\varphi^*(r)$ is obtained by setting $q = 1$.

To validate these theoretical constructs, we also compute the screened electrostatic potential directly from MD trajectories, fully accounting for the Coulombic interactions among all particles and thereby capturing the collective screening effect imposed by the surrounding ionic environment. Taking a sodium cation as a reference, we evaluated the electrostatic potential $\phi_{\text{Na}}(r)$ as a function of distance from the ion. As shown in Fig. 6, the resulting potential profile exhibits a decaying oscillatory behavior with a characteristic period of approximately 2 Å, corresponding to a wave number of 3 Å^{-1} . This characteristic length—identical to that observed in the oscillatory part of h_{ij} , aligns with the collective structural properties of the network between water molecules.

Importantly, this periodicity remains largely unchanged across different electrolyte concentrations, though the amplitude of oscillations decreases with increasing concentration attributed to enhanced ion-ion interactions and screening. From the screened Coulomb potential formula Eq. (17) we know that $\phi_{\text{Na}}(r)$ is obtained from $\varphi^*(r)$ when the dressed-ion charge density $\rho_{\text{Na}}^*(r)$ is used as the source of the potential, taking the place of the test charge distribution $\rho^{\text{ext}}(r)$.

Now, for comparison, let us consider a singled-out ion in an electrolytic solution and calculate the potential created by it

in linear response approximation, using Eq. (53) together with a few model approximations for $\rho^{\text{ext}}(r)$. Firstly, we consider the point charge (PC) model, wherein the ion is treated as a structureless point source of charge. As shown in Fig. 6 (red curves), this model produces significantly stiffer potential profiles, with unrealistic short-range oscillations. This discrepancy stems from the neglect of the finite spatial extent of real ionic charge distributions and seemingly pronounced nonlinear response effects manifested in the simulation results.

To incorporate finite ion size, the Born sphere (BS) model assumes the ionic charge is uniformly distributed over a thin spherical shell of radius a (see Appendix C for details). The resulting screened potential (blue dashed curves in Fig. 6) exhibits smoother behavior and reduced oscillation amplitudes relative to the PC model. Nonetheless, substantial deviations from the MD results persist. Despite incorporating ionic size, the BS model is still fundamentally rooted in linear dielectric theory, and it therefore fails to capture nonlinear and nonlocal electrostatic responses intrinsic to real molecular systems. But, as in the PC-model, this is not the whole story. Oscillations are the result of the dielectric overscreening effect, which in essence is a result of a resonance between the typical harmonics of $\rho^{\text{ext}}(r)$ distribution and the spatial "eigen modes" of water response. Smearing $\rho^{\text{ext}}(r)$ about the spherical shell will dampen that resonance.

In reality, quantum mechanical effects—such as anisotropic orbitals and radial charge delocalization—render this picture oversimplified. To account for these effects, one can introduce the smeared Born sphere (SBS) model, which distributes the ionic charge smoothly over a finite radial width. As shown in Fig. 6, this model significantly reduces the overscreening resonance, bringing the potential distribution closer to MD results. This suppression of overscreening was demonstrated long ago for models of $\chi(k) = 1 - 1/\varepsilon(k)$ that involve overscreening resonance in Ref. [104]. Nevertheless, deviations at short distances remain significant, as nonlinear dielectric response and excluded volume effects—absent in linear response theory—become increasingly important [44]. At larger distances, however, these nonlinearities are less significant, and the SBS model aligns better with MD results, as shown in all panels of Fig. 6.

The application of DIT will be able to account for nonlinear and excluded-volume effects that are not captured by linear response theory. While its practical implementation involves additional complexity, these effects are significant and warrant dedicated investigation. This final subsection has demonstrated their importance and an understanding of when they could be neglected.

V. CONCLUSION AND OUTLOOK

In this study, we employed molecular dynamics simulations to systematically investigate the static nonlocal dielectric function $\varepsilon(k)$ and pair distribution functions of aqueous electrolytes across a range of concentrations, with particular focus on implications of $\varepsilon(k)$ for electrostatic screening. Our results complement and extend the earlier work of Becker *et al.* [78] who primarily analyzed the dipole contribution to the nonlocal dielectric response while treating the ionic degrees of freedom approximately. In contrast, we explicitly include the ionic

response and, for the first time, to our knowledge, connect it to DIT formalism for electrolytes with molecular solvent. This unified treatment offers new insights into both the qualitative and quantitative behavior of screening mechanisms in such systems, in particular as regards the ion-ion correlations and intermolecular interactions in the solutions.

At moderate to large wave numbers k ($> 1 \text{ \AA}^{-1}$) and for electrolyte concentrations up to 1 M, the screening response function, $\chi(k)$, is largely governed by the solvent. The presence of ions leads only to modest modifications in this regime, notably a slight reduction—on the order of a few percent—of the overscreening resonance peak observed in pure water near $k \approx 3 \text{ \AA}^{-1}$. While at higher concentrations (e.g., 3.60 M), more pronounced deviations emerge. The extension of dielectric overscreening to smaller k values suggests possible formation of spatial structures within the ionic subsystem that are not simply aligned with the hydrogen-bonded network of the water solvent.

As a general property of any ionic conductor, $\varepsilon(k)$ must diverge as $\propto 1/k^{-2}$ in the small- k limit for nonzero electrolyte concentrations. The previously suggested ansatz $\varepsilon(k) \approx \varepsilon_{\text{solv}}(k) + \kappa_{D,0}^2/k^2$ —where $\varepsilon_{\text{solv}}(k)$ is the dielectric function of the pure solvent and $\kappa_{D,0}$ the inverse Debye length in vacuum—is shown to be an exact limiting law at infinite dilution of the electrolytes and is valid primarily for dilute solutions. Extensions of this model to more concentrated electrolytes have been obtained by invoking the concept of dressed ion charges, as formalized in Eq. (22). Nevertheless, the limited accuracy of our simulations at small wave numbers precludes definitive conclusions from our simulation in this regime.

Simulations of the macroscopic dielectric constant as a function of electrolyte concentration, calculated from the distribution of dipoles, qualitatively reproduce known experimental trends, lending additional confidence to the employed methodology. The limitations of the use of such a dielectric constant in electrolyte solutions are analyzed.

In the dilute to moderately concentrated regime, the ion-ion correlation functions are well described by an oscillatory term, which is nearly independent of concentration, together with a concentration-dependent Debye-type monotonic term. The oscillatory features mirror those of the bound charge oscillations induced by water dipoles, indicating that water structure dictates ion behavior—apart from the Debye screening—for these concentrations. However, this structural alignment diminishes above approximately 2 M, pointing to increasing independence of ionic correlations from the solvent's structural ordering.

At concentrations below about 2 M, the asymptotic decay of correlation functions is well-described by the classical Debye screening length, provided that the concentration-dependent macroscopic dielectric constant obtained from simulations is used. This is perhaps the most striking result of this study. Notably, it contrasts with experimental observations that report monotonic tails with significantly longer screening lengths. It is not possible to obtain the long-range exponentially decaying tails seen in the experiments in computer simulations of aqueous NaCl solutions, at least not for the standard force field employed in the present calculations. What is made clear by this study is that the observed

long-range monotonic tails cannot be explained by simple Debye-like screening with modified ionic strength in the simulated system, such as that arising from ion pairing/clustering or other forms of charge renormalization.

The fact that $\kappa \approx \kappa_D$ up to about 2 M for the present system is probably a consequence of a cancellation of the effects of steric and electrostatic ion-ion correlations. For primitive model electrolytes with the same concentrations, the steric correlations dominate for weak electrostatic coupling (small q or large ε), leading to $\kappa > \kappa_D$, while $\kappa < \kappa_D$ for strong electrostatic coupling (large q or small ε) [23,36,101]. The present system corresponds to an intermediate case where $\kappa \approx \kappa_D$.

Our results show that the peak positions in the oscillatory part of the ion-ion correlation functions remain largely independent of electrolyte concentration up to 1.9 M, with only the first peak showing a slight shift. Although the amplitudes vary with concentration, no new structural motifs emerge, reinforcing that electrolyte structure is fundamentally governed by water.

The small- k behavior of $\varepsilon(k)$ and the corresponding long-range screening remain particularly challenging to resolve with high confidence, owing to the inherent limitations of the finite-size of the simulation box. Future studies employing substantially larger simulation volumes—potentially achievable on next-generation supercomputing platforms—will be crucial for a more reliable characterization of long-wavelength correlations in highly concentrated electrolytes.

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DATA AVAILABILITY

The data are not publicly available. The data are available from the authors upon reasonable request.

APPENDIX A: SUSCEPTIBILITY CALCULATION

For a classical system, the dielectric response function can be determined based on Eq. (13). In simulation, the bound charge density $\hat{\rho}_b(\mathbf{k})$ (denoted $\hat{\rho}_{b,\mathbf{k}}$ in the main text) is calculated as

$$\hat{\rho}_b(\mathbf{k}) = \frac{1}{\sqrt{V}} \sum_{j,\alpha} z_\alpha e^{-i\mathbf{k} \cdot (\mathbf{r}_j + \delta \mathbf{r}_{j,\alpha})}, \quad (\text{A1})$$

where the summation is over all molecular positions $\mathbf{r}_j$ and the spatial coordinates of molecular sites $\delta \mathbf{r}_{j,\alpha}$. Here, z_α represents the partial charge of site α .

Generally, the bound charge density can be approximately related to the site-site pair correlation function, $H_{ij}(k)$, such that

$$\langle \hat{\rho}_{b,i}(\mathbf{k}) \hat{\rho}_{b,j}(-\mathbf{k}) \rangle = z_i z_j H_{ij}(k), \quad (\text{A2})$$

where z_i is the partial charge, and $\hat{\rho}_{b,i}(\mathbf{k})$ the Fourier transform of the fluctuating atomic charge density of the charge carrying group i .

However, the precision of this approach is often insufficient for accurate calculations of the structure factor in the small k domain. To address this, we calculate the bound charge density $\hat{\rho}_b(\mathbf{r})$ directly in real space for the entire system. The FFT is then used to compute $\hat{\rho}_b(\mathbf{k})$ and $\hat{\rho}_b(-\mathbf{k})$ in Fourier space at each timestep. Statistical averaging is performed over different timesteps, whereby the charge structure factor $\Omega(k)$ in Eq. (14) and the dielectric response function $\chi(k)$, via Eq. (13), are subsequently determined.

APPENDIX B: POLARIZATION RESPONSE FUNCTIONS AND DRESSED PARTICLES

Here, we will consider two kinds of polarization response functions that give the polarization charge density in terms of the electrostatic potential from a charge density $\rho^{\text{ext}}(\mathbf{r})$ and link them to the concept of dressed particles. First, let us consider the potential $\phi_{\mathbf{k}}^{\text{ext}} = \rho_{\mathbf{k}}^{\text{ext}} \phi_k$, that is, the potential from ρ^{ext} in vacuum (i.e., the potential for $\mathbf{D}$). In linear response theory, the polarization charge density ρ^{pol} due to a small ρ^{ext} is given by

$$\rho_{\mathbf{k}}^{\text{pol}} = \Lambda(k) \phi_{\mathbf{k}}^{\text{ext}}, \quad (\text{B1})$$

where Λ is the response function that gives ρ^{pol} as the polarization response to the potential ϕ^{ext} that is also small. It is well-known that this function is equal to $-\Omega(k)/[k_B T]$ (it is a consequence of the FDT), that is, $\Lambda(k) = -\Omega(k)/[k_B T]$.

The other kind of polarization response function is Λ^* , which is the linear response function that gives ρ^{pol} as the polarization response to the total potential ϕ , that is, the potential from both ρ^{ext} and the polarization ρ^{pol} . This relationship is expressed as

$$\rho_{\mathbf{k}}^{\text{pol}} = \Lambda^*(k) \phi_{\mathbf{k}} \quad (\text{B2})$$

for small $\phi_{\mathbf{k}}$.

Now, since $\phi_{\mathbf{k}}^{\text{ext}} = \rho_{\mathbf{k}}^{\text{ext}} \phi_k = \rho_{\mathbf{k}}^{\text{ext}} 4\pi/k^2 = \varepsilon(k) \phi_{\mathbf{k}}$, where we have used Eq. (7), we see from Eq. (B1) that $\rho_{\mathbf{k}}^{\text{pol}} = \Lambda(k) \phi_{\mathbf{k}}^{\text{ext}} = \Lambda(k) \varepsilon(k) \phi_{\mathbf{k}}$, so we can identify $\Lambda^*(k) = \Lambda(k) \varepsilon(k)$. It follows that Eq. (13) can be written as

$$\chi(k) = 1 - \frac{1}{\varepsilon(k)} = -\frac{4\pi \Lambda(k)}{k^2} = -\frac{4\pi \Lambda^*(k)}{\varepsilon(k) k^2}, \quad (\text{B3})$$

which implies that

$$1 = \frac{1}{\varepsilon(k)} \left[1 - \frac{4\pi \Lambda^*(k)}{k^2} \right].$$

This is Eq. (18).

The concept of a *dressed particle* with charge density ρ_j^* can be defined from [34,46,49,51]

$$\rho_{j,\mathbf{k}}^* = \rho_{j,\mathbf{k}}^{\text{tot}} - \Lambda^*(k) \phi_{j,\mathbf{k}}, \quad (\text{B4})$$

where the last term subtracts the *linear part* of the polarization charge density due to the total electrostatic potential ϕ_j from the j particle, that is, ϕ_j given by Eq. (15). This linear part is obtained from Eq. (B2) as applied to the potential ϕ_j , which is *not* small close to the particle. The charge density ρ_j^{tot} contains also the polarization charge from the *nonlinear* electrostatic

response and the polarization due to nonelectrostatic interactions between the particle and the surrounding medium. These latter parts constitute accordingly the charge density ρ_j^{dress} of the dress of the j particle. Recall that $\rho_j^* = \rho_j^{\text{int}} + \rho_j^{\text{dress}}$ and $\rho_j^{\text{tot}} = \rho_j^{\text{int}} + \rho_j^{\text{cloud}}$, so $\rho_j^{\text{dress}} = \rho_j^{\text{cloud}} - \Lambda^*(k)\phi_{j,\mathbf{k}}$.

Equation (15) gives $\phi_{j,\mathbf{k}} = \rho_{j,\mathbf{k}}^{\text{tot}}/k^2 = 4\pi\rho_{j,\mathbf{k}}^{\text{tot}}/k^2$ and by inserting this into Eq. (B4) and using Eq. (18) we obtain $\rho_{j,\mathbf{k}}^* = \rho_{j,\mathbf{k}}^{\text{tot}} [1 - 4\pi\Lambda^*(k)/k^2] = \rho_{j,\mathbf{k}}^{\text{tot}} \varepsilon(k)$, which was used as the definition of $\rho_{j,\mathbf{k}}^*$ in the main text [below Eq. (16)].

The response function $\Lambda(k)$ can be written as

$$\Lambda(k) = -\frac{1}{k_B T} \sum_j n_j \langle \rho_{j,\mathbf{k}}^{\text{int}} \rho_{j,-\mathbf{k}}^{\text{tot}} \rangle_\theta = -\frac{\Omega(k)}{k_B T}, \quad (\text{B5})$$

where the sum is the charge-charge structure factor [cf. Eq. (14)]. By multiplying by $\varepsilon(k)$ we obtain Eq. (19) since $\Lambda^*(k) = \Lambda(k)\varepsilon(k)$ and $\rho_{j,\mathbf{k}}^* = \rho_{j,\mathbf{k}}^{\text{tot}}\varepsilon(k)$.

APPENDIX C: ION FORM-FACTOR MODELS AND SCREENED ELECTROSTATIC POTENTIALS

We present here various models for $\rho^{\text{ext}}(r)$ that are used in Sec. III F. The PC model assumes that $\rho^{\text{ext}}(r)$ is a point charge q at the ion center. In the BS model, the ionic charge q is instead uniformly distributed over a thin spherical shell of radius a :

$$\rho^{\text{ext}}(r) = \rho^{\text{BS}}(r) \equiv \frac{q}{4\pi a^2} \delta(r - a), \quad (\text{C1})$$

where $\delta(r)$ is the radial Dirac function. The function $\rho^{\text{ext}}(r)$ has the Fourier transform,

$$\rho_k^{\text{ext}} = \tilde{\rho}^{\text{BS}}(k) \equiv q \frac{\sin(ka)}{ka}. \quad (\text{C2})$$

Substituting it into Eq. (53), the electrostatic potential becomes

$$\phi(r) = q \frac{2}{\pi} \int_0^\infty \frac{dk}{\varepsilon(k)} \frac{\sin(kr)}{kr} \frac{\sin(ka)}{ka}. \quad (\text{C3})$$

In the SBS model, the ionic charge is smoothly distributed over a layer of finite radial width:

$$\rho_k^{\text{ext}}(r) = \rho^{\text{SBS}}(r) \equiv \frac{q}{4\pi} \frac{\exp\left\{-\frac{|r-a|}{\eta}\right\}}{\eta \left[a^2 + \eta^2 \left(2 - \exp\left(-\frac{a}{\eta}\right)\right)\right]}, \quad (\text{C4})$$

which leads to

$$\rho_k^{\text{ext}} = \tilde{\rho}^{\text{SBS}}(k) \equiv q \frac{\frac{a \sin(ka)}{k} + \eta^2 \frac{2 \cos(ka) - \exp\left(-\frac{a}{\eta}\right)}{1 + \eta^2 k^2}}{\left[a^2 + \eta^2 \left(2 - \exp\left(-\frac{a}{\eta}\right)\right)\right] (1 + \eta^2 k^2)}. \quad (\text{C5})$$

Note that both the BS and SBS models, when substituted into Eq. (53), invoke the so-called immerse charge approximation, within which the test charge is "embedded" within the solvent, inducing dielectric polarization, but without perturbing the structural organization of the solvent itself [104] apart from the induced electrostatic polarization.

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