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Nonlocal electrostatics in ionic liquids: the key to an understanding of the screening decay length and screened interactions.

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Abstract

Screened electrostatic interactions in ionic liquids are investigated by means of exact statistical mechanical analysis combined with physical arguments that enhance the transparency and conceptual accessibility of the analysis and results. The constituent ions and immersed particles in the liquid can have arbitrary shapes and any internal charge distributions. The decay of the screened electrostatic potential and the free energy of interaction in ionic liquids can be exponentially damped oscillatory (like in molten simple salts) as well as plain exponential and long-ranged (like in dilute electrolyte solutions). Both behaviors are in agreement with the exact statistical mechanical analysis and reasons for their appearances are investigated. Exact but surprisingly simple expressions for the decay parameter κ of the screened electrostatics are obtained, which replace the classical expression for the Debye-Hückel parameter κ_{DH} (the reciprocal Debye length). The expressions are applicable both for cases with plain exponential and oscillatory behaviors. The key importance of nonlocal electrostatics is thereby demonstrated explicitly. Dielectric properties of ionic liquids and other electrolytes are investigated, in particular the static dielectric function $\tilde{\epsilon}(k)$ and some effective relative permittivities ($\mathcal{E}_r^{\mathrm{eff}}$ and $\mathcal{E}_r^*$), which take roles that the dielectric constant ε_r has for polar liquids consisting of electroneutral molecules. The dielectric constant in the latter case, which is the limit of $\tilde{\epsilon}(k)$ when the wave number $k \to 0$, can be expressed solely in terms of dipolar features of the molecules. In contrast to this, the effective dielectric permittivities of ionic liquids have contributions also from quadrupolar, octupolar and higher multipolar features of the constituent ions. The "dielectric constant" of electrolytes does not exist since $\tilde{\epsilon}(k) \to \infty$ when $k \to 0$, a well-known effect of perfect screening. The effective relative permittivities $\mathcal{E}_r^{\mathrm{eff}}$ and $\mathcal{E}_r^*$ of ionic liquids are obtained from the non-diverging part of $\tilde{\epsilon}(k)$, but not as a $k \to 0$ limit. Influences of ion associations, especially pairing, are investigated for screened electrostatics and these permittivities. A general, multipolar expansion of $\tilde{\epsilon}(k)$ is derived and used to analyze dielectric properties of ionic liquids and other electrolytes.

I. INTRODUCTION

Ionic liquids are organic salts that are in the liquid state at or near room temperature (at least below 100 °C). They have many unique properties, for instance as solvents, including negligible vapor pressure, high charge density, tunable polarity and high thermal, chemical and electrochemical stability. Therefore, they have been given many important uses including several new, innovative ones. For example, they are used in batteries, super-capacitors and solar cells, as solvents for dispersions of colloids and in organic synthesis, as lubricants, extraction liquids and self-assembly media. For reviews of properties and several uses of ionic liquids see Refs. [1–5]. From a fundamental point of view, the understanding of their properties on the molecular level have given rise to many challenges, not least regarding the dielectric and electrostatic screening characteristics.[2, 6–14] The latter are of key importance for several of the unique features of ionic liquids.

Like in other electrolytes, the situation in an ionic liquid is that the electrostatic potential from a charged particle immersed in the liquid decays in an exponential or exponentially damped oscillatory manner at sufficient distance from the particle provided that the non-electrostatic interactions between the ions are short ranged. Close to the particle, the potential varies in a more complicated manner and contains several exponentially decaying contributions as well as contributions with other functional forms. The exponential screening length of the decay, denoted λ, refers to the leading term at large distances (i.e., with the largest decay length), whether the decay is a plain exponential or an exponentially damped oscillatory one. In molten simple salts the oscillatory decay is the norm.

When the screened electrostatic interaction dominates, the free energy of interaction (the potential of mean force) between two particles in an electrolyte has the same decay length as the mean electrostatic potential and for the oscillatory case, also the same wave length. This is true also for the interaction between two surfaces in contact with the electrolyte. The latter can, for example, be measured experimentally by a surface force apparatus or an atomic force microscope. In many cases the measured force in ionic liquids is damped oscillatory with oscillations detected for several nm,[3, 15–18] but long-ranged monotonic exponential decay like in a dilute electrolyte solution has also been observed with decay length of 4 – 11 nm.[19–21] The latter is very interesting and has give rise to some controversy,[22–24] but the existence of the long-ranged monotonic exponential decay has very recently been verified experimentally for ionic liquids and concentrated electrolyte solutions.[25]

How can it be possible to have a long-ranged monotonic exponential decay in a dense, strongly coupled electrolyte like an ionic liquid? It has been suggested[19] that the ionic liquid in such cases is "an effectively neutral, coordinated cation–anion network (i.e., like 'solvent molecules') that exists in equilibrium with a small fraction of effectively dissociated ions." A possibility is also that many ions in an ionic liquid form ion pairs and only a small fraction of the ions remain dissociated. A coarse-grained model of ion pairing in approximate density functional theory[14] shows that such a pairing can give monotonic exponential decay for the long-range tails of the electrostatic surface forces in ionic liquids. On the theme of ion pairing, an approximate analysis of the static dielectric properties of ionic liquids and fused salts has recently been done by simulations[13] by comparing an ionic fluid with a dipolar fluid that is formed by pairing anions and cations together into dipolar dumbbell particles.

Ideally, a proper analysis of the various possible behaviors of ionic liquids should be done by careful investigation of the statistical mechanics of dense electrolytes without relying on approximations. Since we are only considering equilibrium properties, equilibrium statistical mechanics can be used. In a separate paper, Ref. [26], electrostatic double layer interactions between surfaces immersed in ionic liquids and other electrolytes are investigated. There it is shown by an exact statistical mechanical analysis that strong ion-ion correlations can give rise to monotonic exponential decay with a long decay length in dense electrolytes. Such a decay can, for example, arise from anion-cation associations of various kinds, for instance transient ion pairing or association caused by many-body correlations. The analysis shows that ion pairing is a possibility but not a necessity for monotonic exponential decay to occur. In the present work we will investigate screened electrostatic interactions in bulk electrolytes, thereby continuing and deepening the exact analysis. The properties of the bulk phase is fundamental for an understanding of the long-range distance dependence of interactions between surfaces immersed in a liquid. The decay behavior is determined by the surrounding bulk liquid.

An important question is how to treat the dielectric properties of ionic liquids, in particular what entity plays a role corresponding to the dielectric constant ε_r of pure polar fluids. Since ionic liquids are conductors, the concept of dielectric constant cannot be taken over unchanged because ε_r is infinitely large in this case. For a polar liquid without ions, ε_r equals the limiting value of the static dielectric function $\tilde{\epsilon}(k)$ when the wave number $k \to 0$, i.e. $\varepsilon_r = \tilde{\epsilon}(0)$, but for an electrolyte $\tilde{\epsilon}(k)$ diverges to infinity like $1/k^2$ when $k \to 0$. The dielectric properties and the screening behavior are intimately linked to each other, so in a statistical mechanical analysis both have to be treated simultaneously. As we will see, the dielectric behavior at *nonzero* wave number is important in general.

In many cases the thinking and analyses of electrostatic interactions and the screening phenomenon in ionic liquids have been based on mean-field theories of electrolytes, in particular the Poisson-Boltzmann (PB) approximation and its linearized version the Debye-Hückel (DH) approximation. In these approximations the decay length is equal to the Debye length $\lambda_{\rm DH} = \kappa_{\rm DH}^{-1}$, where $\kappa_{\rm DH}$ is the Debye-Hückel screening parameter as defined from

$$\kappa_{\rm DH}^2 = \frac{\beta}{\varepsilon_0} \sum_l n_l^{\rm b} q_l^2, \tag{1}$$

with $\beta = (k_B T)^{-1}$, k_B Boltzmann's constant, T the absolute temperature, ε_0 the permittivity of vacuum, q_l the charge of an ion of species l and $n_l^{\rm b}$ the number density of this species, where superscript b stands for bulk. The sum is over all species l in the liquid. When the ions are located in a dielectric medium modeled as a continuum with static dielectric constant ε_r, the Debye-Hückel parameter is given by

$$\kappa_{\rm DH}^2 = \frac{\beta}{\varepsilon_r \varepsilon_0} \sum_l n_l^{\rm b} q_l^2 \quad \text{(in dielectric medium)}. \tag{2}$$

This expression for the decay parameter is correct for an electrolyte solution in a solvent with dielectric constant ε_r in the limit of infinitely low concentration, where the ion-ion correlations are very weak since the interionic distances are very large. The conditions in an ionic liquid are, of course, very different from such a solution. The ions are very close together, they correlate strongly with each other and there is no solvent. In ionic liquids, $\kappa_{\rm DH}$ is large and the Debye length very small since $n_l^{\rm b}$ is large; $\kappa_{\rm DH}$ is simply not a relevant quantity.

The exact analysis of classical statistical mechanics for electrolytes shows that the decay parameter κ for the electrostatic screening can be expressed as

$$\kappa^2 = \frac{\beta}{\mathcal{E}_r^* \varepsilon_0} \sum_l n_l^{\rm b} q_l q_l^*, \tag{3}$$

where $\mathcal{E}_r^*$ is a kind of effective relative permittivity and q_l^* is a "renormalized" charge of ions of species l. These are the *only differences compared to the PB expression* (2) – a perhaps surprising result considering the complex situation in a dense ionic liquid. The appearance of $\mathcal{E}_r^*$ and q_l^* is precisely what is needed to accommodate the theoretical treatment of screened interactions to the experimental observations for ionic liquids.

The charge q_l^* in Eq. (3) is the sum of the bare charge q_l and the integral of a charge density surrounding the ion and associated with it. Note that one cannot include the whole ion cloud of the ion to obtain a renormalized charge. The entire ion cloud has a charge that is equal to $-q_l$ (due to local electroneutrality) so it would yield zero when added to q_l. Instead one takes a well-defined part of the ion cloud (a charge density called the "dress" of the ion), which together with the bare charge yields the charge q_l^*. Depending on the conditions, q_l^* can can be quite large or small; it can even change sign.

A crucial feature of the exact theory is that $\mathcal{E}_r^*$ is a function of κ, $\mathcal{E}_r^* = \mathcal{E}_r^*(\kappa)$, so Eq. (3) is actually an equation for κ. This equation has several solutions and each solution gives an exponentially decaying term in the electrostatic interaction potentials with, in general, different decay lengths. The leading term for large distances is the one with the largest decay length $\lambda = \kappa^{-1}$ (the smallest κ value). In some cases more than one term is needed to describe the decay, but in other cases the leading term gives a good description of the decay even at rather small distances. In fact, Eq. (3) applies also when the electrostatic interactions decay in an oscillatory, exponentially damped fashion. This equation then has complex-valued solutions, which gives such behavior of the decay (the real part of κ gives the exponential decay and imaginary part the wave number of the oscillation). In this case there is normally a layering of the ions near a particle or surface into alternating anion-rich and cation-rich layers, leading to an oscillation in sign of the charge density and the electrostatic potential. The plain exponential and the oscillatory cases are accordingly different aspects of the screening of electrostatic interactions; they are closely related to each other and described by the same equation. The experimental surface force results described above are in agreement with a dominance of screened electrostatic interactions in the long-range decay.

The analysis in the current work is done for ionic liquids and electrolyte solutions where the constituent molecules/ions have arbitrary shapes and internal charge distributions. The particles are for simplicity assumed to be rigid and not polarizable. The expressions obtained for the long-range part of the decay in the analysis in this paper are valid provided that the screened electrostatic interactions are dominant for large separations in the liquid (the general theory is, however, not limited to such cases). Furthermore, conditions close to critical points of the fluid are avoided. Under these conditions analysis is exact, i.e., it is done without any approximations. The explicit derivations in this paper are mainly done for cases with plain exponential decay, but as we will see, the end results are equally applicable to oscillatory, exponentially damped decay, which is prevalent in molten salts and ionic liquids.

Since the analysis is exact, it covers a wide variety of different scenarios regarding the details of the local structure in the liquid phase. If, for example, the electrostatic potential decays slower than the extent of a locally ordered structure caused, for example, by specific short-ranged interactions, the conditions above are fulfilled. The measured decay length of the exponentially decaying surface forces of Refs. [19, 21] is of the order of $4 - 11$ nm, so such a locally ordered structure, if it exists, can be pretty extended in this case and still be smaller than the decay length. When such structures exist, the correlations within and between various structures influences the screening length and can make it large.

A major topic in the present work is an investigation of various aspects of the dielectric features of ionic liquids, in particular $\tilde{\epsilon}(k)$. Like the dielectric constant ε_r of a polar liquid, the effective relative permittivity $\mathcal{E}_r^*$ of an ionic liquid is determined by the liquid's dielectric properties. We will find that both quantities are defined from the "regular" part, $\tilde{\epsilon}_{\mathrm{reg}}(k)$, of the dielectric function, which is obtained by removing the part of $\tilde{\epsilon}(k)$ that diverges (a constant divided by k^2). The divergent part is, of course, not present for polar liquids without ions, but it is, for example, present in pure water due to its self-ionization. In electrolytes, $\mathcal{E}_r^*$ is *not* given by the value of $\tilde{\epsilon}_{\mathrm{reg}}(0)$, i.e., the Fourier component at infinite wave length (which is appropriate for a slowly varying potential like $1/r$ for large distances r). The exponential decay of the potential (plain or oscillatory) implies, as we will see, that $\mathcal{E}_r^*$ equals the component of $\tilde{\epsilon}_{\mathrm{reg}}$ at a length scale corresponding to the exponential decay length given by κ.

Key aspects of the analysis in this work are stated in terms of nonlocal electrostatics, which for weak fields can be expressed in terms of the dielectric function. Theories of nonlocal electrostatics have previously been employed mainly for aqueous systems, see for example Refs. [27–33] and references therein. Many of them essentially focus on the wavenumber dependence of $\tilde{\epsilon}(k)$ of the solvent and often also on a position dependence of the dielectric permittivity, thereby mimicking nonlinear polarization effects, for instance near surfaces. The objectives and scopes of these approximate theories of nonlocal electrostatics differ a lot from the focus of the current work.

The present paper is based on the Dressed Ion Theory (DIT),[34–36] an exact formalism for electrostatic interactions in electrolyte solutions in the primitive model, and its extension Dressed Molecule Theory,[37–39] which includes effects of molecular solvent (if present) and is not restricted to spherical ions. In the current paper we will call both of these theories DIT, which is appropriate since we are dealing with ionic liquids. Here we will express the basis of DIT in a new, much simpler and more physical manner than has been done previously and make some significant extensions of this theory. In the simplified derivations in the current work we will, however, use some assumptions that are not needed in general, which will be commented on in the text and in notes. For a more complete exposition of the basis of DIT see the references mentioned above.

It is important to note that DIT is a reformulation of statistical mechanics that gives tools for an understanding of mechanisms in electrolytes and exact relationships between various entities. To obtain numerical results one needs input of data from computer simulations or from approximative theories like density functional theory or integral equations. The latter can be augmented by various theoretical devices in order to treat ionic associations more correctly in dense electrolytes, see for example Ref. [40].

The layout of the paper is as follows. In section II we start for simplicity with systems containing spherical ions and introduce the basis of DIT, focusing on the origin and implications of nonlocal electrostatics in electrolytes, whereby the concept of dressed ions, the polarization response and the dielectric function are treated. Starting from an analysis of $\tilde{\epsilon}(k)$, we thereafter give a general derivation of Eq. (3) for κ, define $\mathcal{E}_r^*$ and analyze the decay of the screened Coulomb potential, whereby we introduce $\mathcal{E}_r^{\text{eff}}$, another effective permittivity. $\mathcal{E}_r^*$ is then investigated for the case of simple electrolytes with ion pairing. In section III, systems with ions of arbitrary internal charge distribution and shape are treated – a task that by necessity is more complicated due to the orientational degrees of freedom of the molecules. The relationship between nonlocal electrostatics and DIT is explored for this case, polarization and screened electrostatic potential are investigated, and multipolar screened interactions between ions are examined. The link between the dielectric constant ε_r of a pure polar liquid and $\mathcal{E}_r^*$ and $\mathcal{E}_r^{\text{eff}}$ for electrolytes is investigated, and the multipolar contributions to $\mathcal{E}_r^*$ and $\tilde{\epsilon}(k)$ are treated in some detail. Simplified expressions for $\mathcal{E}_r^*$ in certain cases are derived based on an analysis of the multipolar terms. The more technical aspects of the derivations in this paper are allocated to two Appendices. Appendix A is devoted to the case of spherical ions and in Appendix B various expansions of the dielectric function $\tilde{\epsilon}(k)$ are derived, including multipolar expansions. An analogous expansion of the reciprocal function $1/\tilde{\epsilon}(k)$ is also derived.

II. SYSTEMS WITH SPHERICAL IONS

We first consider a bulk fluid consisting of spherical anions and cations with point charge at the center of the sphere. The ions can be hard or soft spheres of any sizes; the nonelectrostatic interactions are assumed to have a short range.[41]

A. Polarization response and screened Coulomb potential

1. *Some basics*

Let us initially place the origin of the coordinate system at the center of an i ion, which we will call "the central ion." Due to the interactions between this ion and the other ions, the ionic number densities deviate from the bulk values in the neighborhood of the ion. The number density of ions of species j at distance r from the center of the ion is equal to $n_j^{\mathrm{b}} g_{ij}(r)$, where $g_{ij}(r)$ is the pair distribution functions (radial distribution function) for species i and j. The average charge density $\rho_i(r)$ around the i ion is equal to

$$\rho_i(r) = \sum_j q_j n_j^{\mathrm{b}} g_{ij}(r) = \sum_j q_j n_j^{\mathrm{b}} e^{-\beta w_{ij}(r)}, \tag{4}$$

where we have introduced the pair potential of mean force $w_{ij}(r)$ that satisfies $g_{ij}(r) = \exp(-\beta w_{ij}(r))$. One often describes the varying ion densities around the ion as an "ion cloud" with charge density $\rho_i(r)$.

The average electrostatic potential $\psi_i(r)$ from the i ion and the surrounding charge density $\rho_i(r)$ is according to Coulombs law equal to

$$\psi_i(r) = q_i \phi_{\mathrm{Coul}}(r) + \int d\mathbf{r}' \rho_i(r') \phi_{\mathrm{Coul}}(|\mathbf{r} - \mathbf{r}'|), \tag{5}$$

where $\phi_{\mathrm{Coul}}(r) = 1/(4\pi\varepsilon_0 r)$, $\mathbf{r} = (x, y, z)$ and $r = |\mathbf{r}|$. The integration is taken over the whole space (in this paper, all integrations without explicit limits are taken over all possible values of the respective variables). We can alternatively write this as

$$\psi_i(r) = \int d\mathbf{r}' \rho_i^{\mathrm{tot}}(r') \phi_{\mathrm{Coul}}(|\mathbf{r} - \mathbf{r}'|), \tag{6}$$

where we have introduced the total charge density ρ_i^{tot} of the i ion and its cloud

$$\rho_i^{\mathrm{tot}}(r) = q_i \delta^{(3)}(r) + \rho_i(r) \tag{7}$$

with $\delta^{(3)}(r)$ being the three-dimensional Dirac delta function and $q_i \delta^{(3)}(r)$ the point charge at the origin expressed as a density. The potential ψ_i satisfies Poisson's equation

$$-\varepsilon_0 \nabla^2 \psi_i(r) = \rho_i^{\mathrm{tot}}(r), \tag{8}$$

where $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ is the Laplace operator. Due to the spherical symmetry we can write this as

$$-\varepsilon_0 \frac{1}{r}\frac{\partial^2}{\partial r^2}\left[r\psi_i(r)\right] = \rho_i^{\mathrm{tot}}(r). \tag{9}$$

The boundary conditions at $r \to \infty$ is $\psi_i(r) \to 0$.

In the Poisson-Boltzmann approximation one assumes that the mean field approximation

$$w_{ij}(r) = q_j\psi_i(r) \quad \text{(PB)} \tag{10}$$

is valid for r larger than the distance of closest approach of the i and j ions. The ions are here assumed to have hard cores so for smaller r where the cores overlap, w_{ij} is infinite. The notation (PB) means that the equation is valid only in the PB approximation. The (nonlinear) PB equation can be obtained by combining Eqs. (4), (7), (8), and (10).

A key assumption in the PB approximation is that the correlations between the ions in the ion cloud are entirely neglected. This means that the central ion (here of species i) is treated in a different manner than the rest of the ions. The correlations between the central ion and the rest *are* included, but all other correlations are neglected. All ions apart from the central ion are treated as point ions that do not correlate with each other. This introduces an asymmetry in the treatment of the ions and since $\psi_i(r)/q_i$ is not the same as $\psi_j(r)/q_j$ in general, we have $w_{ij}(r) \neq w_{ji}(r)$, a well known fact. This deviates from the correct relationship $w_{ij}(r) = w_{ji}(r)$. In a correct treatment of the system all ions should in principle be handled on an equal basis and those of the same kind must be treated in the same manner.

2. *Nonlocal electrostatics and dressed ions*

The assumption $w_{ij}(r) = q_j\psi_i(r)$ in the PB approximation implies that the density of j ions at coordinate $\mathbf{r}$ is solely determined by the electrostatic potential ψ_i at the same coordinate, i.e., it is assumed that there is an *entirely local electrostatics*. In reality, the average density of j ions at $\mathbf{r}$ (both of the same and opposite species as the central ion) is influenced by the electrostatic potential ψ_i in an entire neighborhood of this point. Ions at various coordinates $\mathbf{r}'$ in the neighborhood of the point $\mathbf{r}$ are affected by the electrostatic potential and since they correlate with any ion at $\mathbf{r}$, i.e., they influence the probability for ions to be there, the density at $\mathbf{r}$ is affected by the potential at all points $\mathbf{r}'$. This means that in reality there is *nonlocal electrostatics*. For ionic liquids, in particular, it is vital to include the correlations between the ions since the density is very high.

Let us first investigate how the ion-ion correlations can be properly included for large r, i.e., in the tails of $w_{ij}(r)$ and $\rho_i(r)$ far from the central ion, where the electrostatic potential from this ion is weak. We restrict ourselves to cases where the electrostatic interactions constitute the longest range effects, so the electric field due to the central ion and its ion cloud determines the leading contribution to the tail of $w_{ij}(r)$. Since w_{ij} at coordinate $\mathbf{r}$ depends on the potential ψ_i in an entire neighborhood, w_{ij} is, in mathematical terms, a *functional* of ψ_i. Provided r is sufficiently large, $\psi_i(r)$ is so small that we are in the linear response regime, implying that w_{ij} is a *linear* functional of ψ_i. Therefore, we can write

$$w_{ij}(r) \sim \int d\mathbf{r}'\psi_i(r')\rho_j^*(|\mathbf{r}-\mathbf{r}'|), \quad r \to \infty, \tag{11}$$

where ρ_j^* is a function that is as yet unknown and the symbol $\sim$ means "decays asymptotically as." (Mathematically, the existence and uniqueness of such a function follow from Rietz' representation theorem for linear functionals,[42] so Eq. (11) is exact in the limit $r \to \infty$.) We use the notation ρ_j^* since this function has the unit "charge per volume," as follows from an analysis of the units in the equation. The physical role of ρ_j^* in Eq. (11) is to interact with the potential ψ_i as an "effective" charge distribution associated with the j ion. In the integral, the values of ψ_i at various points $\mathbf{r}'$ affect the value of w_{ij} at coordinate $\mathbf{r}$ via the factor $\rho_j^*(|\mathbf{r}-\mathbf{r}'|)$, which is non-zero for a range of $|\mathbf{r}-\mathbf{r}'|$ values.

For large r where $w_{ij}(r)$ is small, we can expand the exponential in Eq. (4) in a power series and retain terms up to the linear one, $\exp[-\beta w_{ij}(r)] \sim 1-\beta w_{ij}(r)$. If we introduce this in Eq. (4), insert Eq. (11) and use $\sum_j q_j n_j^{\mathrm{b}} = 0$ (due to electroneutrality), we obtain

$$\rho_i(r) \sim -\beta \sum_j q_j n_j^{\mathrm{b}} \int d\mathbf{r}'\psi_i(r')\rho_j^*(|\mathbf{r}-\mathbf{r}'|) = \int d\mathbf{r}'\psi_i(r')\chi^*(|\mathbf{r}-\mathbf{r}'|), \quad r \to \infty, \tag{12}$$

where

$$\chi^*(r) = -\beta \sum_j q_j n_j^{\mathrm{b}} \rho_j^*(r). \tag{13}$$

The function χ^* determines, according to Eq. (12), the charge density ρ_i due to the potential ψ_i in the linear regime, i.e., for small ψ_i. This charge density can be described as the polarization response of the bulk electrolyte due to an electrostatic potential, so χ^* is a *polarization response function* in linear response theory (it is closely related to the electric susceptibility and the dielectric function of the fluid). This will be investigated in more detail later.

For smaller r the electrostatic potential $\psi_i(r)$ is not small, so the polarization charge density is not linearly related to $\psi_i(r)$ and the integral in the right hand side (rhs) of Eq. (12) does not give the full charge density $\rho_i(r)$; it only gives the *linear part* of the response to ψ_i. Let us consider the remainder of $\rho_i(r)$ when the linear part has been removed, i.e.,

$$\rho_i(r) - \int d\mathbf{r}' \psi_i(r')\chi^*(|\mathbf{r}-\mathbf{r}'|) \equiv \rho_i^{\text{dress}}(r), \tag{14}$$

which we denote $\rho_i^{\text{dress}}(r)$ for reasons to be explained later. It is equal to the charge density that arises from the nonlinear part of the response to the electrostatic potential and, in addition, from any non-electrostatic effects that influence the density around the central ion, like hard core exclusion and core-core correlations.

We will now reformulate Poisson's equation (8). Let us insert the definition of ρ_i^{tot}, Eq. (7), in the rhs and subtract the integral in Eq. (14) from both sides. Poisson's equation becomes

$$-\varepsilon_0 \nabla^2 \psi_i(r) - \int d\mathbf{r}' \psi_i(r')\chi^*(|\mathbf{r}-\mathbf{r}'|) = q_i \delta^{(3)}(r) + \rho_i^{\text{dress}}(r). \tag{15}$$

The solution $\psi_i(r)$ to this equation can be written

$$\begin{aligned}\psi_i(r) &= \int d\mathbf{r}'' \left[q_i \delta^{(3)}(r'') + \rho_i^{\text{dress}}(r'')\right] \phi^*_{\text{Coul}}(|\mathbf{r}-\mathbf{r}''|), \\ &= q_i \phi^*_{\text{Coul}}(r) + \int d\mathbf{r}'' \rho_i^{\text{dress}}(r'') \phi^*_{\text{Coul}}(|\mathbf{r}-\mathbf{r}''|),\end{aligned} \tag{16}$$

where the function $\phi^*_{\text{Coul}}(r)$, called the (normalized) *Screened Coulomb potential*, satisfies

$$-\varepsilon_0 \nabla^2 \phi^*_{\text{Coul}}(r) - \int d\mathbf{r}' \phi^*_{\text{Coul}}(r')\chi^*(|\mathbf{r}-\mathbf{r}'|) = \delta^{(3)}(r). \tag{17}$$

One can show that Eq. (16) is the solution of Eq. (15) by direct insertion, whereby Eq. (17) is used to simplify the result. Note that Eq. (16) has the same general form as Eq. (5).

Mathematically, the definition of $\phi^*_{\text{Coul}}(r)$ in Eq. (17) means that it is a Green's function. Its physical meaning is that it expresses the propagation of the total electrostatic field (the so-called Maxwell field) including the effect of polarization of the medium to linear order. Since the electrostatic field near an ion is strong, the nonlinear polarization must also be included and this is done for $\psi_i(r)$ via the term with ρ_i^{dress} in Eq. (16). By replacing the central i ion and its surrounding ion cloud by a "leaner" entity given by the *dressed ion* with charge density $q_i\delta^{(3)}(r) + \rho_i^{\text{dress}}(r)$, we can hence use the screened Coulomb potential to calculate the total potential from Eq. (16). This equation has the same form as Coulomb's law, but with the screened (ϕ^*_{Coul}) rather than the unscreened (ϕ_{Coul}) Coulomb potential.

Now, a very important result of DIT[35] is that the effective charge distribution ρ_j^* that interacts with the potential according to Eq. (11) is *exactly the same* as the dressed ion charge distribution, i.e.,

$$\rho_j^*(r) = q_j \delta^{(3)}(r) + \rho_j^{\text{dress}}(r). \tag{18}$$

This means that Eq. (16) can be written

$$\psi_i(r) = \int d\mathbf{r}'\rho_i^*(r')\phi_{\text{Coul}}^*(|\mathbf{r}-\mathbf{r}'|), \tag{19}$$

which should be compared to Eq. (6). Thus the dressed ion is an entity that has the dual role as (i) the charge density that via the screened Coulomb potential ϕ_{Coul}^* gives rise to the electrostatic potential $\psi_i(r)$ (for all r) and (ii) the the charge density that interacts with $\psi_i(r)$ giving the potential of mean force w_{ij} in the tail region (for large r). If we define the screened electrostatic pair interaction

$$w_{ij}^{\text{el}}(r_{12}) = \int d\mathbf{r}_3 d\mathbf{r}_4 \rho_i^*(r_{13})\phi_{\text{Coul}}^*(r_{34})\rho_j^*(r_{24}), \tag{20}$$

for all r_{12}, where $r_{ij} = |\mathbf{r}_{ij}|$ and $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$, it follows from Eq. (11) and (19) that

$$w_{ij}(r_{12}) \sim w_{ij}^{\text{el}}(r_{12}), \quad r_{12} \to \infty. \tag{21}$$

These relationships are perfectly symmetric in i and j in agreement with the fact that $w_{ij} = w_{ji}$. Due to the symmetry we also have [cf. Eq. (11)]

$$w_{ij}(r) \sim \int d\mathbf{r}'\rho_i^*(r')\psi_j(|\mathbf{r}-\mathbf{r}'|), \quad r \to \infty.$$

The screened electrostatic pair interaction w_{ij}^{el} is, in fact, a contribution to w_{ij} that is relevant for all distances and not only large ones.[43] The asymptotic decay analyses in this paper are valid provided that the electrostatic interaction w_{ij}^{el} is the contribution to w_{ij} with the longest range; we only consider cases where ϕ_{Coul}^* decays slower than ρ_l^* for all l. This restriction is, however, not needed in general. In fact, in almost all cases when $w_{ij}(r)$ decays in a plain exponential or exponentially damped oscillatory manner, it is the decay of electrostatics (via $\phi_{\text{Coul}}^*(r)$) that determines the leading contribution to $w_{ij}(r)$ for large r.[44]

Eq. (11) is a special case of the completely general functional derivative result

$$\frac{\delta W_j(\mathbf{r})}{\delta \Psi(\mathbf{r}')} = \rho_j^*(\mathbf{r}'|\mathbf{r}) \tag{22}$$

for the potential of mean force W_j in an inhomogeneous liquid exposed to a total electrostatic field Ψ (see Ref. [37] where ρ_j^* is denoted ρ_j^0). Here $\rho_j^*(\mathbf{r}'|\mathbf{r})$ is the dressed ion charge density at $\mathbf{r}'$ for a particle located at $\mathbf{r}$ as defined from the distribution functions for particles in the liquid.[37] This functional derivative formula means that $\delta W_j(\mathbf{r}) = \int d\mathbf{r}'\delta\Psi(\mathbf{r}')\rho_j^*(\mathbf{r}'|\mathbf{r})$ for the variation δW_j when the total electrostatic field is varied by $\delta\Psi$. For the special case in

Eq. (11), the (weak) potential of mean force w_{ij} plays the role of δW_j, the (weak) electrostatic potential ψ_i is $\delta\Psi$ is and one can identify $\rho_j^*(|\mathbf{r}-\mathbf{r}'|)$ with $\rho_j^*(\mathbf{r}'|\mathbf{r})$.

The dressed ion charge density $\rho_i^*(r)$ and the response function $\chi^*(r)$, which play crucial roles in the current theory,[45] can be obtained from other functions like $g_{ij}(r)$ and $\rho_i^{\text{tot}}(r)$ that are directly accessible via numerical calculations using, for example, computer simulations or integral equation theories. Some ways to do this are briefly outlined in Appendix A 1.

3. *The dielectric function*

Let an external electrostatic field $\mathbf{E}^{\text{ext}}(\mathbf{r})$ polarize an unperturbed bulk fluid. This field originates from some fixed charges that in principle are not part of the system. The external field gives rise to a polarization charge density $\rho^{\text{pol}}(\mathbf{r})$ and a total electrostatic field $\mathbf{E}(\mathbf{r})$, which is the sum of $\mathbf{E}^{\text{ext}}$ and the field from ρ^{pol}. The total field is sometimes called the Maxwell field and $\mathbf{E}^{\text{ext}}$ can alternatively be expressed in terms of the displacement field $\mathbf{D}$ given by $\mathbf{D}(\mathbf{r}) = \mathbf{E}^{\text{ext}}(\mathbf{r})/\varepsilon_0$, but we will use $\mathbf{E}^{\text{ext}}$ here. The two fields can be expressed in terms of the respective electrostatic potentials $\mathbf{E}^{\text{ext}}(\mathbf{r}) = -\nabla\Psi^{\text{ext}}(\mathbf{r})$ and $\mathbf{E}(\mathbf{r}) = -\nabla\Psi(\mathbf{r})$. We have

$$\Psi(\mathbf{r}) = \Psi^{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}'\rho^{\text{pol}}(\mathbf{r}')\phi_{\text{Coul}}(|\mathbf{r}-\mathbf{r}'|). \tag{23}$$

For the unperturbed fluid (in absence of $\mathbf{E}^{\text{ext}}$) these potentials are set to zero by default.

We will now consider the situation with a weak external field, so the polarization charge density is given by linear response. Using the response function $\chi^*(r)$ we have

$$\rho^{\text{pol}}(\mathbf{r}) = \int d\mathbf{r}'\Psi(\mathbf{r}')\chi^*(|\mathbf{r}-\mathbf{r}'|) \quad \text{(weak field)}. \tag{24}$$

By inserting this in Eq. (23) and taking the Fourier transform, whereby the convolution integrals become products in Fourier space, we obtain

$$\tilde{\Psi}(\mathbf{k}) = \tilde{\Psi}^{\text{ext}}(\mathbf{k}) + \tilde{\Psi}(\mathbf{k})\tilde{\chi}^*(k)\tilde{\phi}_{\text{Coul}}(k) \quad \text{(weak field)}, \tag{25}$$

where $\tilde{\Psi}(\mathbf{k}) = \int d\mathbf{r}\Psi(\mathbf{r})\exp(-i\mathbf{k}\cdot\mathbf{r})$, and $k = |\mathbf{k}|$. The Fourier transform of χ^* is given by

$$\tilde{\chi}^*(k) = \int d\mathbf{r}\frac{\sin(kr)}{kr}\chi^*(r) \tag{26}$$

since $\chi^*(r)$ is radially symmetric and $\tilde{\phi}_{\text{Coul}}(k) = 1/(\varepsilon_0 k^2)$.

Eq. (25) can be written

$$\Psi(\mathbf{k}) = \frac{\Psi^{\text{ext}}(\mathbf{k})}{\tilde{\epsilon}(k)} \quad \text{(weak field)}, \tag{27}$$

where

$$\tilde{\epsilon}(k) = 1 - \tilde{\chi}^*(k)\tilde{\phi}_{\text{Coul}}(k) \tag{28}$$

is the static dielectric function expressed in $\tilde{\chi}^*$ (more precisely the static *longitudinal* dielectric function). By inserting the Fourier transform of Eq. (13) we obtain $\tilde{\epsilon}(k)$ expressed in terms of $\tilde{\rho}_i^*(k)$, see Eq. (A5). In Appendix A 2, $\tilde{\epsilon}(k)$ is also expressed in other, more common forms.

The dielectric function can be split into two parts. Eq. (28) can be written as

$$\begin{aligned}\tilde{\epsilon}(k) &= 1 - \frac{\tilde{\chi}^*(k)}{\varepsilon_0 k^2} = 1 - \frac{\tilde{\chi}^*(k) - \tilde{\chi}^*(0)}{\varepsilon_0 k^2} - \frac{\tilde{\chi}^*(0)}{\varepsilon_0 k^2} \\ &= \tilde{\epsilon}_{\text{reg}}(k) + \tilde{\epsilon}_{\text{sing}}(k)\end{aligned} \tag{29}$$

where

$$\tilde{\epsilon}_{\text{sing}}(k) = -\frac{\tilde{\chi}^*(0)}{\varepsilon_0 k^2} \tag{30}$$

is singular when $k \to 0$ and

$$\tilde{\epsilon}_{\text{reg}}(k) = 1 - \frac{\tilde{\chi}^*(k) - \tilde{\chi}^*(0)}{\varepsilon_0 k^2} = 1 - \frac{1}{\varepsilon_0}\int d\mathbf{r}\, r^2 \left[\frac{\sin(kr) - kr}{(kr)^3}\right] \chi^*(r) \tag{31}$$

is regular (non-singular) at $k = 0$, where it equals

$$\tilde{\epsilon}_{\text{reg}}(0) = 1 - \frac{1}{6\varepsilon_0}\int d\mathbf{r}\, r^2 \chi^*(r).$$

Using Eq. (13) we can write Eq. (30) as

$$\tilde{\epsilon}_{\text{sing}}(k) = \frac{\beta}{\varepsilon_0}\sum_l n_l^{\text{b}} q_l q_l^* \frac{1}{k^2}, \tag{32}$$

where

$$q_l^* = \int d\mathbf{r} \rho_l^*(r) = \tilde{\rho}_l^*(0) \tag{33}$$

is the total charge of a dressed ion of species l, i.e., the bare charge q_l plus the charge of the dress. Note that while $\int d\mathbf{r}\rho_l^{\text{tot}}(r) = 0$ due to local electroneutrality, we have $q_l^* = \int d\mathbf{r}\rho_l^*(r) \neq 0$ in general. This follows since $\rho_l^{\text{tot}}(r)$ and $\rho_l^*(r)$ differ by the linear part of the polarization response, which has a total charge that normally is nonzero. It is, however, possible for each q_l^* to change sign as a function of the system parameters (e.g. temperature or density), but q_l^* for all species are in general not exactly equal to zero simultaneously.

The divergence of $\tilde{\epsilon}(k)$ at $k = 0$ is a consequence of the fact that the electrolyte is a conductor and we see that the singular part $\tilde{\epsilon}_{\text{sing}}$ is intimately connected to the values of the dressed ion charges q_l^*. Alternatively, the coefficient in front of $1/k^2$ can be expressed in terms of ρ_l^{tot}, see Appendix A 1, Eq. (A9).

The screened Coulomb potential $\phi^*_{\text{Coul}}(r)$, which is defined by Eq. (17), can be expressed as follows in Fourier space. From the Fourier transform of this equation we obtain

$$\tilde{\phi}^*_{\text{Coul}}(k) = \frac{\tilde{\phi}_{\text{Coul}}(k)}{1 - \tilde{\chi}^*(k)\tilde{\phi}_{\text{Coul}}(k)} \tag{34}$$

(note that ∇^2 gives a factor $(\mathrm{i}\mathbf{k})^2 = -k^2$ in Fourier space). By using Eq. (28) we see that

$$\tilde{\phi}^*_{\text{Coul}}(k) = \frac{\tilde{\phi}_{\text{Coul}}(k)}{\tilde{\epsilon}(k)} = \frac{1}{\varepsilon_0 k^2 \tilde{\epsilon}(k)}, \tag{35}$$

where the first equality should be compared with Eq. (27).

B. Screening behavior and the leading decay length

In the PB approximation $\chi^*(r) = -\varepsilon_0 \kappa^2_{\text{DH}} \delta^{(3)}(r)$ and $\tilde{\epsilon}(k) = 1 + \kappa^2_{\text{DH}}/k^2$. The screened Coulomb potential ϕ^*_{Coul} in this approximation equals

$$\phi^*_{\text{Coul}}(r) = \frac{e^{-\kappa_{\text{DH}} r}}{4\pi\varepsilon_0 r} \quad \text{(PB)}.$$

In the general, exact case it has been shown[35] that this kind of decay of the potential holds for large r provided that the electrostatic coupling is sufficiently weak, but with a different decay parameter κ and pre-factor A

$$\phi^*_{\text{Coul}}(r) \sim A \frac{e^{-\kappa r}}{r}, \quad r \to \infty \tag{36}$$

[the coefficient A will be specified later, see Eq. (45)]. For higher coupling, the potential is oscillatory and there is also a sinusoidal factor, see below.

The following results (in the present Section II B) are presented for the case of spherical ions, but they are, in fact, of general validity as will be apparent later in Section III (the same applies to the results in the preceding Section II A 3).

1. The equation for κ

We now have all that is needed to derive an exact equation for the decay parameter κ. When $r > 0$ Eq. (17) equals

$$-\varepsilon_0 \frac{1}{r} \frac{\partial^2}{\partial r^2} \left[r \phi^*_{\text{Coul}}(r) \right] = \int d\mathbf{r}' \phi^*_{\text{Coul}}(r') \chi^*(|\mathbf{r} - \mathbf{r}'|).$$

For large r, we can insert the limiting form (36) for $\phi^*_{\rm Coul}(r)$ on both sides (note that χ^* has a shorter range than $\phi^*_{\rm Coul}$). By performing the derivatives in the left hand side (lhs), we obtain

$$\begin{aligned}-\varepsilon_0\kappa^2 A\frac{e^{-\kappa r}}{r} &\sim \int d\mathbf{r}' A\frac{e^{-\kappa r'}}{r'}\chi^*(|\mathbf{r}-\mathbf{r}'|)\\ &= \int dr''(r'')^2\left[\int d\hat{\mathbf{r}}'' A\frac{e^{-\kappa|\mathbf{r}-\mathbf{r}''|}}{|\mathbf{r}-\mathbf{r}''|}\right]\chi^*(r'') \qquad (37)\end{aligned}$$

for large r, where we have made the variable substitution $\mathbf{r}''=\mathbf{r}-\mathbf{r}'$ to obtain the last equality. We have also separated the radial integration over r'' in spherical polar coordinates and the integration over the azimuthal and polar angles (φ''_r,θ''_r) of $\mathbf{r}''$. The latter are represented by the unit vector $\hat{\mathbf{r}}''=\mathbf{r}''/r''$.

We now make use of the mathematical identity

$$\int d\hat{\mathbf{r}}''\,\frac{e^{-\kappa|\mathbf{r}-\mathbf{r}''|}}{|\mathbf{r}-\mathbf{r}''|} = 2\pi\frac{e^{-\kappa|r-r''|}-e^{-\kappa|r+r''|}}{\kappa r r''} = 4\pi\frac{e^{-\kappa r}}{r}\,\frac{\sinh(\kappa r'')}{\kappa r''}, \qquad (38)$$

where the last equality holds when $r>r''$ (in our case $r\gg r''$), and obtain from Eq. (37)

$$-\varepsilon_0\kappa^2 A\frac{e^{-\kappa r}}{r} \sim 4\pi A\frac{e^{-\kappa r}}{r}\int dr''(r'')^2\frac{\sinh(\kappa r'')}{\kappa r''}\chi^*(r'').$$

An identification of the coefficients on either side gives after simplification

$$-\varepsilon_0\kappa^2 = \int d\mathbf{r}''\frac{\sinh(\kappa r'')}{\kappa r''}\chi^*(r''), \qquad (39)$$

where $d\mathbf{r}''=dr''(r'')^2 4\pi$ (spherical symmetry).[46] Given the function χ^*, we can use this equation to determine κ. The unknown variable, κ, appears on both sides of the equation which can be solved for κ (at least numerically). The function χ^* is independent of κ but is, of course, dependent on the state of the system.

By using Eq. (26) and the identity $\sinh(x)=\sin(\mathrm{i}x)/\mathrm{i}$, where i is the imaginary unit (distinguish between i and the species index i), we can express the rhs of Eq. (39) as $\tilde{\chi}^*(\mathrm{i}\kappa)$, so the equation can be written as $-\varepsilon_0\kappa^2=\tilde{\chi}^*(\mathrm{i}\kappa)$. From the expression (28) for $\tilde{\epsilon}(k)$ we can conclude that $\tilde{\epsilon}(\mathrm{i}\kappa)=1-\tilde{\chi}^*(\mathrm{i}\kappa)\tilde{\phi}_{\rm Coul}(\mathrm{i}\kappa)=1+\tilde{\chi}^*(\mathrm{i}\kappa)/(\varepsilon_0\kappa^2)=0$, so Eq. (39) is equivalent to $\tilde{\epsilon}(\mathrm{i}\kappa)=0$. Therefore, we have

$$\tilde{\epsilon}(\mathrm{i}\kappa)=\tilde{\epsilon}_{\rm reg}(\mathrm{i}\kappa)+\tilde{\epsilon}_{\rm sing}(\mathrm{i}\kappa)=\mathcal{E}^*_r(\kappa)-\frac{\beta}{\varepsilon_0\kappa^2}\sum_l n_l^{\rm b}q_l q_l^*=0,$$

where we have defined

$$\begin{aligned}\mathcal{E}^*_r(\kappa) &\equiv \tilde{\epsilon}_{\rm reg}(\mathrm{i}\kappa)\\ &= 1+\frac{1}{\varepsilon_0}\int d\mathbf{r}\, r^2\left[\frac{\sinh(\kappa r)-\kappa r}{(\kappa r)^3}\right]\chi^*(r) \qquad (40)\end{aligned}$$

and used Eqs. (31) and (32). Thus we conclude that Eq. (39) is equivalent to

$$\kappa^2 = \frac{\beta}{\mathcal{E}_r^* \varepsilon_0} \sum_l n_l^{\mathrm{b}} q_l q_l^*, \tag{41}$$

where $\mathcal{E}_r^* = \mathcal{E}_r^*(\kappa)$. The similarity between Eqs. (2) and (41) is obvious. The rhs of Eq. (41) depends on κ via $\mathcal{E}_r^*$, while the dressed ion charge q_l^* is independent of the parameter κ (but q_l^* depends, of course, on the state of the system).

For a thin plasma at high temperatures κ is small so $\mathcal{E}_r^* \approx \tilde{\epsilon}_{\mathrm{reg}}(0) = 1$ and $q_j^* \approx q_j$, which implies $\kappa \approx \kappa_{\mathrm{DH}}$ and the PB result, Eq. (1), is recovered in the limit $\kappa \to 0$. Likewise, κ is small for a dilute electrolyte solution so $\mathcal{E}_r^* \approx \tilde{\epsilon}_{\mathrm{reg}}(0) \approx \varepsilon_r$, the dielectric constant for the solvent, and $q_j^* \approx q_j$. Thus, the PB result Eq. (2) is obtained in the limit of infinite dilution.

It is here appropriate to make a comment on the extension of the Fourier transform to complex k values, which is done here by simply inserting $k = \mathrm{i}\kappa$ into its definition. For a function $f(r)$ we have

$$\tilde{f}(k) = \int d\mathbf{r} e^{-ik\hat{\mathbf{k}}\cdot\mathbf{r}} f(r) = \int d\mathbf{r} \frac{\sin(kr)}{kr} f(r),$$

so therefore

$$\tilde{f}(\mathrm{i}\kappa) = \int d\mathbf{r} e^{\kappa\hat{\mathbf{k}}\cdot\mathbf{r}} f(r) = \int d\mathbf{r} \frac{\sinh(\kappa r)}{\kappa r} f(r), \tag{42}$$

i.e., a kind of Laplace transform. The extension of $\tilde{\chi}^*(k)$, $\tilde{\epsilon}(k)$ et cetera to complex k values is motivated by the fact that the decay in the electrolyte is exponential, so the exponential and hyperbolic functions are appropriate. For example in $\mathcal{E}_r^* = \tilde{\epsilon}_{\mathrm{reg}}(\mathrm{i}\kappa)$ one extracts (via the Laplace transform) the component of the dielectric response of the electrolyte that is relevant for the exponential decay at the length scale given by the decay length.

2. Solutions to the equation for κ

In the limit of zero ionic density and/or infinite temperature $\kappa = \kappa_{\mathrm{DH}}$ is a solution to Eq. (39). Otherwise $\kappa \neq \kappa_{\mathrm{DH}}$. In fact, Eq. (39) has in the general case more than one solution κ, κ' etc. and each solution corresponds to a term like in Eq. (36), so if we consider the two solutions with smallest κ values we have

$$\phi^*_{\mathrm{Coul}}(r) \sim A\frac{e^{-\kappa r}}{r} + A'\frac{e^{-\kappa' r}}{r}, \tag{43}$$

where $\kappa < \kappa'$. The first term is dominating at large r – it gives the leading asymptotic contribution – and the second term contributes significantly for smaller r. The leading decay length is given by $\lambda = \kappa^{-1}$. The electrostatic potential ψ_i from an i ion and the charge density $\rho_i^{\mathrm{tot}}(r)$ decays in the same fashion (but multiplied by different coefficients). The presence of these terms are nicely illustrated for high temperature plasmas in the molecular-dynamics simulation by Keblinski et al.[6], see Figure 5c in that paper.

When the density is increased, the two solutions κ and κ' to Eq. (39) approach each other and at one density they become equal, which is nicely illustrated in Figure 5b in Ref. [6]. This density constitutes the cross-over point to oscillatory decay of the potential and charge density. For even higher density, κ and κ' become complex-valued; they are each other's complex conjugates $\kappa = \kappa_{\Re} + \mathrm{i}\kappa_{\Im}$ and $\kappa' = \kappa_{\Re} - \mathrm{i}\kappa_{\Im}$. The prefactors in Eq. (43) become complex valued too (complex conjugates) $A = |A|\exp(-\mathrm{i}\vartheta)$ and $A' = |A'|\exp(\mathrm{i}\vartheta_i)$, where ϑ is a real number and $|A| = |A'| = B/2$, which defines B. The sum of the two terms in Eq. (43) is therefore a real valued function

$$\begin{aligned}\phi^*_{\mathrm{Coul}}(r) &\sim |A|e^{-\mathrm{i}\vartheta}\frac{e^{-(\kappa_{\Re}+\mathrm{i}\kappa_{\Im})r}}{r} + |A'|e^{\mathrm{i}\vartheta}\frac{e^{-(\kappa_{\Re}-\mathrm{i}\kappa_{\Im})r}}{r} \\ &= \frac{B}{2}\left[e^{-\mathrm{i}(\kappa_{\Im}r+\vartheta)} + e^{\mathrm{i}(\kappa_{\Im}r+\vartheta)}\right]\frac{e^{-\kappa_{\Re}r}}{r} \\ &= B\cos(\kappa_{\Im}r+\vartheta)\frac{e^{-\kappa_{\Re}r}}{r}. \end{aligned} \tag{44}$$

In this case the decay length is given by $\lambda = \kappa_{\Re}^{-1}$, the wave length is $2\pi/\kappa_{\Im}$ and ϑ is a phase shift. This is the decay behavior commonly found in molten simple salts. In general there can be more than one pair of complex-valued solutions to Eq. (39) giving other oscillatory contributions but with larger $\kappa_{\Re}$, so they decay more quickly with r. There can also be both plain exponential and oscillatory terms at the same time. In the present work we will mainly consider the leading term, irrespectively whether it is plain exponential or oscillatory.

The cross-over to oscillatory decay is often called the Kirkwood cross-over point, named after John G. Kirkwood who already in the 1930s showed the existence of a transition to oscillatory behavior for electrolytes.[47, 48] The deviation of κ from κ_{DH} and the appearance of oscillatory decay occur in theories that treat all ions in the electrolytes on an equal basis, rather than, as in the PB and DH approximations, treat the central ion in a different manner than the rest of the ions. This is demonstrated in simple fashion in Ref. [49], where it is shown that even a DH-like approximation can give rise to these behaviors if all ions are treated on an equal basis. The same is true in, for example, the Mean Spherical Approximation (MSA),[50] the Modified Poisson-Boltzmann theory by Outhwaite[51, 52] and other fairly simple approximations.[53]

Ever since the work by Kirkwood, several authors have investigated the exponentially decaying contributions, the transition to oscillatory decay and the behaviors of the decay lengths and the wave length for electrolytes with spherical ions. More recently, a detailed analysis of the decay behavior of electrolytes including the Kirkwood cross-over has been made in a Generalized Mean Spherical Approximation by Leote de Carvalho and Evans.[54] For a MC simulation study of the leading terms in the decay behavior of the electrostatic potential and the pair distribution functions see Ref. [55], where also some higher order terms are considered using a DIT analysis. For the dense ionic systems treated in the current paper, the work by Keblinski et al.[6], mentioned above, is particularly relevant. They have made systematic molecular-dynamics simulations for various conditions from the plasma to the molten salt states. One important fact shown in Refs. [6, 55] is that the leading decay term given by Eqs. (36) or (44) gives in many cases a good description down to surprisingly small distances r; in some cases down to a couple of ionic diameters. Thus, the decay behavior given by the leading asymptotic term *is not limited to very large* r. An analysis of the leading decay is therefore of relevance for a large part of the range of the electrostatic interactions.

Let us now consider the decay behavior of $\phi^*_{\text{Coul}}(r)$ in more detail. When the solution κ to Eq. (39) is real, the screened Coulomb potential decays like

$$\phi^*_{\text{Coul}}(r) \sim \frac{e^{-\kappa r}}{4\pi\mathcal{E}_r^{\text{eff}}\varepsilon_0 r}, \qquad r \to \infty, \tag{45}$$

where

$$\mathcal{E}_r^{\text{eff}} = \mathcal{E}_r^{\text{eff}}(\kappa) = \frac{3}{2} + \frac{1}{2\varepsilon_0\kappa^2}\int d\mathbf{r}\,\cosh(\kappa r)\chi^*(r) \tag{46}$$

as shown in Appendix A 3, so $A = [4\pi\mathcal{E}_r^{\text{eff}}\varepsilon_0]^{-1}$. Note that the quantity $\mathcal{E}_r^{\text{eff}}$ is different from $\mathcal{E}_r^*$. Both $\mathcal{E}_r^{\text{eff}}$ and $\mathcal{E}_r^*$ play the role of an effective relative permittivity of the electrolyte and both are expressed in terms of the polarization response function $\chi^*(r)$.

As we have seen, Eq. (39) have in general several solutions, each of which corresponds to a term in ϕ^*_{Coul} like in Eq. (45), but with larger values of κ (shorter decay lengths), cf. Eq. (43). These terms have other values of $\mathcal{E}_r^{\text{eff}} = \mathcal{E}_r^{\text{eff}}(\kappa)$ since these quantities are evaluated at the respective κ value, for example $A' = [4\pi\mathcal{E}_r^{\text{eff}}(\kappa')\varepsilon_0]^{-1}$.[36, 55] Likewise, $\mathcal{E}_r^* = \mathcal{E}_r^*(\kappa)$ has different values for each of the terms. Note that each of the terms in ϕ^*_{Coul} with different decay lengths gives a contribution to ψ_i with the same decay length and likewise a contribution to w_{ij} with this decay length.

When the solution κ of Eq. (39) is complex, the parameter $\mathcal{E}_r^{\text{eff}} = \mathcal{E}_r^{\text{eff}}(\kappa) = \mathcal{E}_r^{\text{eff}}(\kappa_{\Re} \pm \mathrm{i}\kappa_{\Im})$ is also complex so we can write $\mathcal{E}_r^{\text{eff}} = \mathsf{E}_r^{\text{eff}}\exp(\pm\mathrm{i}\vartheta_{\mathsf{E}})$ where $\mathsf{E}_r^{\text{eff}} = |\mathcal{E}_r^{\text{eff}}|$ and ϑ_{E} are real, and we have when $r \to \infty$

$$\phi^*_{\mathrm{Coul}}(r) \sim \frac{e^{-\kappa_{\Re} r}\cos(\kappa_{\Im} r + \vartheta_{\mathsf{E}})}{2\pi \mathsf{E}_r^{\mathrm{eff}} \varepsilon_0 r}, \tag{47}$$

so $B = [2\pi \mathsf{E}_r^{\mathrm{eff}} \varepsilon_0]^{-1}$ and $\vartheta = \vartheta_{\mathsf{E}}$. Here $\mathsf{E}_r^{\mathrm{eff}}$ plays the role of an effective relative permittivity of the electrolyte.

As shown in Appendix A 3, $\mathcal{E}_r^{\mathrm{eff}}$ can be written as

$$\mathcal{E}_r^{\mathrm{eff}}(\kappa) = \left[\tilde{\epsilon}_{\mathrm{reg}}(k) + \frac{k}{2}\frac{d\tilde{\epsilon}_{\mathrm{reg}}(k)}{dk}\right]_{k=\mathrm{i}\kappa}. \tag{48}$$

Thus both $\mathcal{E}_r^*(\kappa)$ and $\mathcal{E}_r^{\mathrm{eff}}(\kappa)$ can be expressed in terms of $\tilde{\epsilon}_{\mathrm{reg}}(k)$. They differ by the second term in the square bracket in Eq. (48). As we have seen, each contribution to $\phi^*_{\mathrm{Coul}}(r)$ with a different decay length has its own values of $\mathcal{E}_r^* = \mathcal{E}_r^*(\kappa)$ and $\mathcal{E}_r^{\mathrm{eff}} = \mathcal{E}_r^{\mathrm{eff}}(\kappa)$ and the absolute values of them has the roles of effective permittivities associated with the contribution.

C. Ion pairing

Let us now consider the possibility of ion pairing. Such pairing in simple electrolytes is in the general case not an actual association of anions and cations; it is rather a question of a large probability for anions and cations to be close together, i.e., that the pair distribution function $g_{lj}(r)$ is very large for r values where the ions are close together. This is due to the anion-cation attraction and the effects of ion-ion correlations. Such strongly peaked pair distribution at close approach is certainly a nonlinear effect and is therefore present in the dressed ion charge distribution $\rho_l^*(r)$; it appears as a peak of charge with a sign opposite to that of q_l. This means that $\rho_l^*(r)$ has a point charge at the center and a very large peak of opposite charge at the anion-cation contact distance for all species involved in ion pairing. It is of course also possible to have a system where non-electrostatic attractions between anions and cations enhance pairing.

Since the present theory is exact, the influence of ion pairing on the value of κ must be contained in the values of $\mathcal{E}_r^*$ and the dressed ion charges q_l^*. All other quantities in the rhs of Eq. (41) are system parameters and hence constants. If there is substantial ion pairing for, say, a 1:1 electrolyte, the dressed ion charges q_+^* and q_-^* will be small since paired ions are in close contact with an ion of opposite charge (included in the dress) forming an electroneutral entity. Paired ions thus do not contribute to q_l^*, which is an average over all ions of species l, while unpaired ions do. It follows from Eq. (41) that small q_l^* values make κ small and hence the decay length large (for details see below).

Furthermore, the pairing affects the value of $\mathcal{E}_r^* = \tilde{\epsilon}_{\mathrm{reg}}(\mathrm{i}\kappa)$. By inserting Eq. (13) into Eq. (48) we can write

$$\mathcal{E}_r^* = 1 - \frac{\beta}{\varepsilon_0} \sum_l q_l n_l^{\mathrm{b}} \int d\mathbf{r}\, r^2 \left[\frac{\sinh(\kappa r) - \kappa r}{(\kappa r)^3} \right] \rho_l^*(r) \tag{49}$$

$$= 1 - \frac{\beta}{\varepsilon_0} \sum_l q_l n_l^{\mathrm{b}} \left(\frac{1}{3!} \int d\mathbf{r}\, r^2 \rho_l^*(r) + \frac{\kappa^2}{5!} \int d\mathbf{r}\, r^4 \rho_l^*(r) + \dots \right) \tag{50}$$

$$= 1 - \frac{\beta}{\varepsilon_0} \sum_l n_l^{\mathrm{b}} \left(\frac{1}{6} q_l m_l^{*(2)} + \frac{\kappa^2}{5!} q_l m_l^{*(4)} + \dots \right), \tag{51}$$

where we have expanded the sinh function in a Taylor series and defined the moments

$$m_l^{*(\nu)} = \int d\mathbf{r}\, r^\nu \rho_l^*(r)$$

of the charge distribution $\rho_l^*(r)$. When κ is small $\mathcal{E}_r^*(\kappa) \approx 1 - \beta \sum_l n_l^{\mathrm{b}} q_l m_l^{*(2)}/(6\varepsilon_0) = \tilde{\epsilon}_{\mathrm{reg}}(0)$.

Consider a symmetric electrolyte with number density $n_+^{\mathrm{b}} = n_-^{\mathrm{b}} = n^{\mathrm{b}}$. Let us assume that the ions have hard cores and say that a fraction ξ of the ions are involved in ion pairing on average. The contribution from the pairs to the peak of opposite charge in $\rho_l^*(r)$ at contact, $r = a$ (the anion-cation contact distance), correspond to a total charge $-\xi q_l$, which we can approximately express as a delta function at $r = a$, namely $-\xi q_l \delta(r-a)/(4\pi a^2)$ written as a three-dimensional charge density ($\delta(x)$ is the one-dimensional Dirac function). When we insert this delta function term in $\rho_l^*(r)$ into the definition of $m_l^{*(2)}$, we obtain the result $-a^2 \xi q_l$. Thus, in Eq. (51) we have a contribution to $\mathcal{E}_r^*$ equal to $\xi\beta \sum_l n_l^{\mathrm{b}} (\mu_l^{\mathrm{pair}})^2/(6\varepsilon_0)$, where $\mu_l^{\mathrm{pair}} = |q_l| a$ is the dipole moment of an ion pair. Since $\mu_+^{\mathrm{pair}} = \mu_-^{\mathrm{pair}} = \mu^{\mathrm{pair}}$ this contribution equals $\xi\beta n^{\mathrm{b}} (\mu^{\mathrm{pair}})^2/(3\varepsilon_0)$, which is independent of κ. As we will see in section III C, where ion pairing is discussed further, this contribution to $\mathcal{E}_r^*$ corresponds to the "self-term" in the dielectric response for a dipolar fluid. Effects of, for example, dipole-dipole and charge-dipole correlations are contained in the remaining contributions to $\mathcal{E}_r^*$ from $\rho_l^*(r)$. Thus, the ion pairing gives rise to contributions to $\mathcal{E}_r^*$ similar to those from a dipolar solvent. Note, however, that *it is not necessary to have an actual pairing* to obtain these relationships. It is sufficient that an ion is surrounded by several ions of opposite sign that it attracts strongly for various reasons – a situation that is encountered many times in a dense ionic liquid.

If the values of q_l^* are sufficiently small, irrespectively of the reason for this, the decay parameter κ is small and hence the decay length large. This can be concluded from Eq. (41), where we can see that $\kappa^2 \to 0$ when $q_l^* \to 0$ for all l, since $\mathcal{E}_r^*$ approaches the finite value $\tilde{\epsilon}_{\mathrm{reg}}(0)$ when $\kappa \to 0$. If $\tilde{\epsilon}_{\mathrm{reg}}(0)$ is large, κ^2 can be small even if the q_l^* values are not very small.

The value of κ^2 depends, of course, also on the higher order terms in Eq. (51), but since their sum is of the order of κ^2, their contribution is not very important for small κ. Thus, small q_l^* values for all l and a large value of $\tilde{\epsilon}_{\text{reg}}(0)$ both favor a large decay length.

III. IONS WITH ANY SHAPE AND ANY INTERNAL CHARGE DISTRIBUTION

In this section we treat bulk fluids consisting of anions and cations of any shape and any internal charge distribution. For simplicity we restrict ourselves to rigid particles that are not polarizable. Our main purpose is to investigate ionic liquids, but the theory is also applicable to electrolyte solutions with a molecular solvent. The charge distribution inside an ionic or polar particle can be a continuous density or a set of point charges (defined by a set of delta functions). For a particle of species i the internal charge density is given by $\sigma_i(\mathbf{r}, \boldsymbol{\omega})$, where $\mathbf{r}$ is counted from the center of mass of the particle and $\boldsymbol{\omega}$ is the particle's orientation described by the three Euler angles (φ, θ, η) in the laboratory frame. For a linear particle only the azimuthal and polar angles (φ, θ) are needed since the third angle, η, is selected as a rotation around the symmetry axis, so it is redundant. We we use $\boldsymbol{\omega} = (\varphi, \cos\theta, \chi)/(8\pi^2)$ and for the linear case $\boldsymbol{\omega} = (\varphi, \cos\theta)/(4\pi)$ as orientational coordinate; both have the property $\int d\boldsymbol{\omega} = 1$.

The total charge of the particle

$$q_i = \int d\mathbf{r} \sigma_i(\mathbf{r}, \boldsymbol{\omega}) \tag{52}$$

is, of course, independent of $\boldsymbol{\omega}$. The dipole moment of the particle is given by

$$\boldsymbol{\mu}_i(\boldsymbol{\omega}) = \int d\mathbf{r}\, \mathbf{r} \sigma_i(\mathbf{r}, \boldsymbol{\omega}) \tag{53}$$

and the quadrupole moment

$$\boldsymbol{\Theta}_i(\boldsymbol{\omega}) = \frac{1}{2} \int d\mathbf{r}\, [3\mathbf{r}\mathbf{r} - r^2 \mathbb{I}] \sigma_i(\mathbf{r}, \boldsymbol{\omega}), \tag{54}$$

where $\mathbb{I}$ is the identity tensor: $\mathbb{I}_{xx} = \mathbb{I}_{yy} = \mathbb{I}_{zz} = 1$ and $\mathbb{I}_{\nu\nu'} = 0$ when $\nu \neq \nu'$ (this definition of quadrupole moment differs by a factor of 1/2 from the definition used, for example, by Gray and Gubbins[56] and Jackson.[57]) The higher multipole moments are defined from

$$\boldsymbol{\mathcal{M}}_i^{(l)}(\boldsymbol{\omega}) = \int d\mathbf{r}\, \mathbf{P}_l(\mathbf{r}) \sigma_i(\mathbf{r}, \boldsymbol{\omega}), \tag{55}$$

where $\mathbf{P}_l(\mathbf{r})$ is a polynomial tensor of order l defined in Appendix B (it is called the Legendre polynomial tensor[58–60] and is symmetric and traceless, see also Ref. [38]). We have $\mathbf{P}_0(\mathbf{r}) = 1$, $\mathbf{P}_1(\mathbf{r}) = \mathbf{r}$ and $\mathbf{P}_2(\mathbf{r}) = [3\mathbf{r}\mathbf{r} - r^2\mathbb{I}]/2$, so $q_i = \boldsymbol{\mathcal{M}}_i^{(0)}$, $\boldsymbol{\mu}_i = \boldsymbol{\mathcal{M}}_i^{(1)}$ and $\boldsymbol{\Theta}_i = \boldsymbol{\mathcal{M}}_i^{(2)}$.

Consider two particles of species i and j with centers of mass at coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ and orientations $\boldsymbol{\omega}_1$ and $\boldsymbol{\omega}_2$, respectively. The pair interaction potential between the particles is

$$u_{ij}(\mathbf{r}_{12},\boldsymbol{\omega}_1,\boldsymbol{\omega}_2) = u_{ij}^{\mathrm{sh}}(\mathbf{r}_{12},\boldsymbol{\omega}_1,\boldsymbol{\omega}_2) + u_{ij}^{\mathrm{el}}(\mathbf{r}_{12},\boldsymbol{\omega}_1,\boldsymbol{\omega}_2),$$

where u_{ij}^{sh} is the non-electrostatic interaction and the electrostatic one is given by

$$u_{ij}^{\mathrm{el}}(\mathbf{r}_{12},\boldsymbol{\omega}_1,\boldsymbol{\omega}_2) = \int d\mathbf{r}_3 d\mathbf{r}_4 \sigma_i(\mathbf{r}_{13},\boldsymbol{\omega}_1)\phi_{\mathrm{Coul}}(r_{34})\sigma_j(\mathbf{r}_{24},\boldsymbol{\omega}_2), \tag{56}$$

as illustrated in Fig. 1. Like before we assume that the non-electrostatic part u_{ij}^{sh} has a short range and is strongly repulsive for small r_{12}. It is otherwise arbitrary.

Figure 1. A sketch of two ions of species i and j placed with their centers of mass at $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively. They have orientations $\boldsymbol{\omega}_1$ and $\boldsymbol{\omega}_2$ and internal charge densities $\sigma_i(\mathbf{r}_{13},\boldsymbol{\omega}_1)$ and $\sigma_j(\mathbf{r}_{24},\boldsymbol{\omega}_2)$, respectively, where each vector $\mathbf{r}_{13}$ and $\mathbf{r}_{24}$ starts at the center of mass of the ion. The charge densities are illustrated as color shades varying between red (positive) and blue (negative). These densities interact via the Coulomb potential $\phi_{\mathrm{Coul}}(r_{34})$, giving the electrostatic interaction $u_{ij}^{\mathrm{el}}(\mathbf{r}_{12},\boldsymbol{\omega}_1,\boldsymbol{\omega}_2)$ between the ions as shown in Eq. (56). An analogous illustration applies to the screened electrostatic part of the potential of mean force $w_{ij}^{\mathrm{el}}(\mathbf{r}_{12},\boldsymbol{\omega}_1,\boldsymbol{\omega}_2)$ between the ions as given in Eq. (71), where the dressed ion charge densities $\rho_i^*(\mathbf{r}_{13},\boldsymbol{\omega}_1)$ and $\rho_j^*(\mathbf{r}_{24},\boldsymbol{\omega}_2)$ interact via the screened Coulomb potential $\phi_{\mathrm{Coul}}^*(r_{34})$. These latter charge densities consist of the charge densities $\sigma_i + \rho_i^{\mathrm{dress}}$ and $\sigma_j + \rho_j^{\mathrm{dress}}$, respectively, and are non-zero both inside and outside of the ions.

The average charge density around an i particle with orientation $\boldsymbol{\omega}_1$ is given by

$$\rho_i(\mathbf{r}_{13},\boldsymbol{\omega}_1) = \sum_j \int d\mathbf{r}_4 d\boldsymbol{\omega}_4 n_j^{\mathrm{b}} g_{ij}(\mathbf{r}_{14},\boldsymbol{\omega}_1,\boldsymbol{\omega}_4)\sigma_j(\mathbf{r}_{43},\boldsymbol{\omega}_4). \tag{57}$$

The total charge density of the particle and its ion cloud is

$$\rho_i^{\mathrm{tot}}(\mathbf{r}_{13},\boldsymbol{\omega}_1) = \sigma_i(\mathbf{r}_{13},\boldsymbol{\omega}_1) + \rho_i(\mathbf{r}_{13},\boldsymbol{\omega}_1) \tag{58}$$

and the average electrostatic potential around the particle equals

$$\psi_i(\mathbf{r}_{13},\boldsymbol{\omega}_1) = \int d\mathbf{r}_4 \rho_i^{\mathrm{tot}}(\mathbf{r}_{14},\boldsymbol{\omega}_1)\phi_{\mathrm{Coul}}(r_{43}). \tag{59}$$

The vector $\mathbf{r}_{13}$ is counted from the center of mass of the i particle in the last three formulas.

A. Polarization response

Let us return to the case treated in Section II A 3, where an external electrostatic field $\mathbf{E}^{\mathrm{ext}}(\mathbf{r}) = -\nabla\Psi^{\mathrm{ext}}(\mathbf{r})$ polarizes an unperturbed bulk liquid and gives rise to a polarization charge density $\rho^{\mathrm{pol}}(\mathbf{r})$. This charge density originates from deviations in particle density from the bulk values n_j^{b} (for all j) caused by the external field and from net orientations of the particles in the field. Say that the resulting number density equals $n_j(\mathbf{r},\boldsymbol{\omega})$, meaning that $n_j(\mathbf{r},\boldsymbol{\omega})d\mathbf{r}d\boldsymbol{\omega}$ is the average number of j particles with orientation within $d\boldsymbol{\omega}$ around $\boldsymbol{\omega}$ and with centers in the volume element $d\mathbf{r}$ around the coordinate $\mathbf{r}$. We have

$$\rho^{\mathrm{pol}}(\mathbf{r}_2) = \sum_j \int d\mathbf{r}_3 d\boldsymbol{\omega}_3 n_j(\mathbf{r}_3,\boldsymbol{\omega}_3)\sigma_j(\mathbf{r}_{32},\boldsymbol{\omega}_3).$$

The total electrostatic potential $\Psi(\mathbf{r})$ is, as before, given by Eq. (23).

The number density n_j can be written in terms of a potential of mean force W_j that satisfies $n_j(\mathbf{r},\boldsymbol{\omega}) = n_j^{\mathrm{b}}\exp(-\beta W_j(\mathbf{r},\boldsymbol{\omega}))$, so we have

$$\rho^{\mathrm{pol}}(\mathbf{r}_2) = \sum_j \int d\mathbf{r}_3 d\boldsymbol{\omega}_3 n_j^{\mathrm{b}} \exp(-\beta W_j(\mathbf{r}_3,\boldsymbol{\omega}_3))\sigma_j(\mathbf{r}_{32},\boldsymbol{\omega}_3). \tag{60}$$

We now consider the case of a weak external field (in the limit of zero field). Then $n_j(\mathbf{r})$ is close to n_j^{b} so $W_j(\mathbf{r})$ is small and the exponential function in Eq. (60) can be expanded to linear order. We obtain

$$\begin{aligned}\rho^{\mathrm{pol}}(\mathbf{r}_2) &= \sum_j \int d\mathbf{r}_3 d\boldsymbol{\omega}_3 n_j^{\mathrm{b}} \left[1-\beta W_j(\mathbf{r}_3,\boldsymbol{\omega}_3)\right]\sigma_j(\mathbf{r}_{32},\boldsymbol{\omega}_3) \\ &= -\beta \sum_j \int d\mathbf{r}_3 d\boldsymbol{\omega}_3 n_j^{\mathrm{b}} W_j(\mathbf{r}_3,\boldsymbol{\omega}_3)\sigma_j(\mathbf{r}_{32},\boldsymbol{\omega}_3) \quad \text{(weak field)}\end{aligned} \tag{61}$$

because $\sum_j \int d\mathbf{r}_3 d\boldsymbol{\omega}_3 n_j^{\mathrm{b}}\sigma_j(\mathbf{r}_{32},\boldsymbol{\omega}_4) = \sum_j n_j^{\mathrm{b}} q_j = 0$ by electroneutrality. The deviation in density from the bulk value and hence the deviation of W_j from zero are due to the interactions of the ions with the total electrostatic potential $\Psi(\mathbf{r})$. Since the electrostatics is nonlocal, as discussed in Section II A 2, and since W_j accordingly is a linear functional of Ψ when the latter is small, we can write

$$W_j(\mathbf{r}_3,\boldsymbol{\omega}_3)=\int d\mathbf{r}_4\Psi(\mathbf{r}_4)\rho_j^*(\mathbf{r}_{34},\boldsymbol{\omega}_3)\quad\text{(weak field)}.\tag{62}$$

(The existence and uniqueness of ρ_j^* follow from Rietz' representation theorem in this case too. See also the comment on the functional derivative $\delta W_j(\mathbf{r})/\delta\Psi(\mathbf{r}')$ in Eq. (22), but the coordinate $\mathbf{r}$ should be replaced by $\mathbf{r},\boldsymbol{\omega}$ in δW_j and ρ_j^* .)

By inserting Eq. (62) into Eq. (61) we can write after a change of the order of integration

$$\rho^{\rm pol}(\mathbf{r}_2)=-\beta\sum_j\int d\mathbf{r}_4\left[\int d\mathbf{r}_3d\boldsymbol{\omega}_3n_j^{\rm b}\rho_j^*(\mathbf{r}_{34},\boldsymbol{\omega}_3)\sigma_j(\mathbf{r}_{32},\boldsymbol{\omega}_3)\right]\Psi(\mathbf{r}_4)\quad\text{(weak field)}$$

and hence we obtain (cf. Eq. (24))

$$\rho^{\rm pol}(\mathbf{r}_2)=\int d\mathbf{r}_4\Psi(\mathbf{r}_4)\chi^*(r_{42})\quad\text{(weak field)}.\tag{63}$$

with χ^* given by

$$\chi^*(r_{42})=-\beta\sum_j\int d\mathbf{r}_3d\boldsymbol{\omega}_3n_j^{\rm b}\rho_j^*(\mathbf{r}_{34},\boldsymbol{\omega}_3)\sigma_j(\mathbf{r}_{32},\boldsymbol{\omega}_3).\tag{64}$$

The function χ^* is spherically symmetric since we have integrated over all orientations $\boldsymbol{\omega}_3$ and since all functions here refer to the properties of a bulk fluid. This relationship constitutes the generalization of Eq. (13), see also Ref. [37].

B. Screened Coulomb interactions and $\tilde{\varepsilon}(k)$

Let us apply these results to the potential ψ_i given by Eq. (59), which satisfies the Poisson equation with $\rho_i^{\rm tot}$ in the rhs (cf. Eq. (8)). We introduce the dress of an ion in the same way as for spherical ions, Eq. (14), by removing the linear part of the response to ψ_i. We thereby obtain the Poisson equation in the form

$$-\varepsilon_0\nabla^2\psi_i(\mathbf{r},\boldsymbol{\omega})-\int d\mathbf{r}'\psi_i(\mathbf{r}',\boldsymbol{\omega})\chi^*(|\mathbf{r}-\mathbf{r}'|)=\sigma_i(\mathbf{r},\boldsymbol{\omega})+\rho_i^{\rm dress}(\mathbf{r},\boldsymbol{\omega}),\tag{65}$$

which has the solution

$$\psi_i(\mathbf{r},\boldsymbol{\omega})=\int d\mathbf{r}'\left(\sigma_i(\mathbf{r}',\boldsymbol{\omega})+\rho_i^{\rm dress}(\mathbf{r}',\boldsymbol{\omega})\right)\phi^*_{\rm Coul}(|\mathbf{r}-\mathbf{r}'|)\tag{66}$$

$$=\int d\mathbf{r}'\rho_i^*(\mathbf{r}',\boldsymbol{\omega})\phi^*_{\rm Coul}(|\mathbf{r}-\mathbf{r}'|)\tag{67}$$

where $\phi^*_{\rm Coul}$ satisfies Eq. (17) like before. In the last equality we have used the fact[37] that ρ^*_i equals the dressed ion charge density also in this case, $\rho^*_i = \sigma_i + \rho^{\rm dress}_i$. Furthermore, the screened Coulomb potential $\phi^*_{\rm Coul}(r)$ decays[37] as in Eq. (45), i.e.,

$$\phi^*_{\rm Coul}(r) \sim \frac{e^{-\kappa r}}{4\pi\mathcal{E}^{\rm eff}_r\varepsilon_0 r}, \qquad r \to \infty \tag{68}$$

when κ is real and as in Eq. (47) when κ is complex.

As mentioned earlier, the results in Sections II A 3 and II B are valid in general. Since $\phi^*_{\rm Coul}(r)$ satisfies Eq. (17) like before, its Fourier transform is given by Eq. (35). The decay parameter κ is still a solution to Eq. (39), which is equivalent to $\tilde\epsilon(\mathrm{i}\kappa) = 0$ and, as we will see, to Eq. (41). Furthermore, $\mathcal{E}^{\rm eff}_r$ is still given by Eqs. (46) and (48).

An explicit expression for the dielectric function $\tilde\epsilon(k)$ can be obtained by inserting the Fourier transform of Eq. (64) into Eq. (28). We obtain

$$\tilde\epsilon(k) = 1 + \frac{\beta}{\varepsilon_0 k^2}\sum_j n^{\rm b}_j \left\langle \tilde\rho^*_j(-\mathbf{k},\boldsymbol{\omega})\tilde\sigma_j(\mathbf{k},\boldsymbol{\omega})\right\rangle_{\boldsymbol{\omega}}, \tag{69}$$

where $\langle\cdot\rangle_{\boldsymbol{\omega}}$ is the average over the orientations (this average is a different way to write the integration over orientations in Eq. (64)) and where $-\mathbf{k}$ appears in $\tilde\rho^*_j$ since the integral in Eq. (64) is not a convolution, but it would be if $\mathbf{r}_{34}$ were replaced by $\mathbf{r}_{43} = -\mathbf{r}_{34}$. Note that the rhs is independent of the direction $\hat{\mathbf{k}}$ of the wave vector $\mathbf{k}$ since the average over $\boldsymbol{\omega}$ is taken.

We have $\tilde\epsilon(k) = \tilde\epsilon_{\rm reg}(k) + \tilde\epsilon_{\rm sing}(k)$ with $\tilde\epsilon_{\rm sing}(k)$ and $\tilde\epsilon_{\rm reg}(k)$ defined as before, Eqs. (30) and (31). For $k = 0$ the sum in Eq. (69) is equal to $\sum_j n^{\rm b}_j q^*_j q_j$, where

$$q^*_j = \tilde\rho^*_j(0,\boldsymbol{\omega}) = \int d\mathbf{r}\,\rho^*_j(\mathbf{r},\boldsymbol{\omega})$$

is the dressed ion charge for the present case (it is, of course, independent of $\boldsymbol{\omega}$), so the expression (32) for $\tilde\epsilon_{\rm sing}(k)$ is valid in general. It follows from the same arguments as in Section II B 1 that the decay parameter κ is a solution to the same exact equation as before $\kappa^2 = \beta\sum_j n^{\rm b}_j q_j q^*_j/[\mathcal{E}^*_r(\kappa)\varepsilon_0]$, Eq. (41). The sum $\sum_j n^{\rm b}_j q^*_j q_j$, which also occurs in the coefficient in front of $1/k^2$ in $\tilde\epsilon_{\rm sing}(k)$, can alternatively be written in terms of various moments of $\rho^{\rm tot}_j$, see Appendix B, Eqs. (B35) and (B36).

The expression for $\mathcal{E}^*_r$ in terms of $\tilde\rho^*_l$ is more complicated than Eq. (49) of the previous case with spherical ions. We can obtain an explicit expression for $\mathcal{E}^*_r$ by removing $\tilde\epsilon_{\rm sing}(k)$ from Eq. (69) and inserting $k = \mathrm{i}\kappa$, whereby it follows that

$$\mathcal{E}^*_r \equiv \tilde\epsilon_{\rm reg}(\mathrm{i}\kappa) = 1 - \frac{\beta}{\varepsilon_0\kappa^2}\sum_j n^{\rm b}_j \left\langle \tilde\rho^*_j(-k\hat{\mathbf{k}},\boldsymbol{\omega})\tilde\sigma_j(k\hat{\mathbf{k}},\boldsymbol{\omega}) - \tilde\rho^*_j(0,\boldsymbol{\omega})\tilde\sigma_j(0,\boldsymbol{\omega})\right\rangle_{\boldsymbol{\omega}}\Big|_{k=\mathrm{i}\kappa}. \tag{70}$$

This relationship will be expressed in a different form below, Eq. (82).

Finally, by applying Eq. (62) to the tail of the pair-potential of mean force w_{ij} between two ions of species i and j separated by $\mathbf{r}_{12}$ and with orientations $\boldsymbol{\omega}_1$ and $\boldsymbol{\omega}_2$, respectively, we obtain (by letting ψ_i take the role of Ψ)

$$w_{ij}(\mathbf{r}_{12},\boldsymbol{\omega}_1,\boldsymbol{\omega}_2) \sim \int d\mathbf{r}_4 \psi_i(\mathbf{r}_{14},\boldsymbol{\omega}_1)\rho_j^*(\mathbf{r}_{24},\boldsymbol{\omega}_2), \quad r_{12} \to \infty.$$

By inserting Eq. (67) into the rhs and defining

$$w_{ij}^{\mathrm{el}}(\mathbf{r}_{12},\boldsymbol{\omega}_1,\boldsymbol{\omega}_2) = \int d\mathbf{r}_3 d\mathbf{r}_4 \rho_i^*(\mathbf{r}_{13},\boldsymbol{\omega}_1)\phi_{\mathrm{Coul}}^*(r_{34})\rho_j^*(\mathbf{r}_{24},\boldsymbol{\omega}_2) \tag{71}$$

for all $\mathbf{r}_{12}$, we can write this as (cf. Eqs. (20) and (21))

$$w_{ij}(\mathbf{r}_{12},\boldsymbol{\omega}_1,\boldsymbol{\omega}_2) \sim w_{ij}^{\mathrm{el}}(\mathbf{r}_{12},\boldsymbol{\omega}_1,\boldsymbol{\omega}_2), \quad r_{12} \to \infty. \tag{72}$$

Thus the ion-ion interaction is given at large distances by the screened Coulomb interaction between the charge distributions of the two dressed ions. As we have seen,[43] w_{ij}^{el} is a contribution to w_{ij} that is relevant for all distances r_{12} and not only large ones. For the cases considered in this paper w_{ij}^{el} dominates at large distances and ϕ_{Coul}^* decays slower than ρ_i^* for all i. As mentioned in the Introduction, the experimental surface forces at large separations are in agreement with a dominance of electrostatics. Eq. (71) has the same form as the Coulomb interaction in Eq. (56) and can be illustrated in the same manner, Fig. 1.

C. The relative permittivities $\mathcal{E}_r^*$ and $\mathcal{E}_r^{\mathrm{eff}}$ vs. the dielectric constant ε_r; ion pairing

As we have seen, the dielectric constant ε_r for a solvent, which appears in the expression (2) for the screening decay length in dilute electrolyte solutions, is replaced by the effective relative permittivity $\mathcal{E}_r^*$ in the corresponding expression (3) for concentrated electrolyte solutions and ionic liquids. The physical meaning of $\mathcal{E}_r^* \equiv \tilde{\epsilon}_{\mathrm{reg}}(\mathrm{i}\kappa)$ can be made clearer by utilizing expansions of $\tilde{\epsilon}(k)$ derived in Appendix B. Let us first consider the Taylor expansion of $\tilde{\epsilon}_{\mathrm{reg}}(k)$ given by Eq. (B23)

$$\tilde{\epsilon}_{\mathrm{reg}}(k) = b_0^* + b_2^* k^2 + b_4^* k^4 + \mathcal{O}(k^6), \tag{73}$$

where (see Eq. (B21))

$$b_0^* = 1 + \frac{\beta}{\varepsilon_0}\sum_j n_j^{\mathrm{b}}\left[\frac{1}{3}\boldsymbol{\mu}_j\cdot\boldsymbol{\mu}_j^* - \frac{1}{6}(q_j m_j^{*(2)} + q_j^* m_j^{(2)})\right] \tag{74}$$

and b_2^* is defined in Eq. (B22) [similar expressions for b_ν^* with $\nu \geq 4$ can be obtained from from Eqs. (B15) and (B19), see Appendix B]. In b_0^* we have

$$\boldsymbol{\mu}_j^*(\boldsymbol{\omega}) = \int d\mathbf{r}\, \mathbf{r} \rho_j^*(\mathbf{r}, \boldsymbol{\omega}),$$

i.e., the dipole moment of the charge distribution ρ_j^*, and

$$\begin{aligned} m_j^{*(2)} &= \int d\mathbf{r}\, r^2 \rho_j^*(\mathbf{r}, \boldsymbol{\omega}) \\ m_j^{(2)} &= \int d\mathbf{r}\, r^2 \sigma_j(\mathbf{r}, \boldsymbol{\omega}), \end{aligned}$$

which are the second moments of the charge distributions ρ_j^* and σ_j, respectively. The dot product $\boldsymbol{\mu}_j \cdot \boldsymbol{\mu}_j^*$ and each second moment are independent of the orientation $\boldsymbol{\omega}$. The symbol $\mathcal{O}(k^\nu)$ in Eq. (73) means k^ν times a function that stays finite when $k \to 0$.

By inserting $k = \mathrm{i}\kappa$ in Eq. (73) we obtain [cf. Eq. (B24)]

$$\mathcal{E}_r^* = \tilde{\epsilon}_{\mathrm{reg}}(\mathrm{i}\kappa) = b_0^* - b_2^*\kappa^2 + b_4^*\kappa^4 + \mathcal{O}(\kappa^6). \tag{75}$$

Note that the term proportional to $q_j m_j^{*(2)}$ in b_0^* is the same as the corresponding term in Eq. (51) for the spherical case (in that case $m_j^{(2)} = 0$ since the ions have only a point charge at the center and $\boldsymbol{\mu}_j = \boldsymbol{\mu}_j^* = 0$). The fourth moment term in Eq. (51) contributes to b_2^*, see Eq. (B22). For cases with very small κ, i.e., when the screening length λ is very long, $\mathcal{E}_r^* \approx b_0^* = \tilde{\epsilon}_{\mathrm{reg}}(0)$. Since [see Eq. (B25)]

$$\mathcal{E}_r^{\mathrm{eff}} = b_0^* - 2b_2^*\kappa^2 + 3b_4^*\kappa^4 + \mathcal{O}(\kappa^6), \tag{76}$$

we also have $\mathcal{E}_r^{\mathrm{eff}} \approx b_0^* = \tilde{\epsilon}_{\mathrm{reg}}(0)$ in such cases.

Let us compare with a nonelectrolyte, where $\tilde{\epsilon}(k) = \tilde{\epsilon}_{\mathrm{reg}}(k)$ and hence where $\lim_{k\to 0} \tilde{\epsilon}(k) = b_0^*$. In this case both q_j and q_j^* are zero for all j and only the first term inside the sum in b_0^* remains (Eq. (74)), so the dielectric constant is

$$\varepsilon_r = \tilde{\epsilon}(0) = 1 + \frac{\beta}{3\varepsilon_0} \sum_j n_j^{\mathrm{b}} \boldsymbol{\mu}_j \cdot \boldsymbol{\mu}_j^* \quad \text{(nonelectrolyte)}. \tag{77}$$

This is a classical expression for ε_r which can, for instance, be found in Refs. [61, 62] for a pure dipole fluid.[63] Note that for cases when the molecules have higher order multipole moments, still only the dipolar term with $\boldsymbol{\mu}_j \cdot \boldsymbol{\mu}_j^*$ contributes to ε_r, a well-known fact. Because $\kappa = 0$ for a nonelectrolyte, we have $\mathcal{E}_r^* = \varepsilon_r$ and $\mathcal{E}_r^{\mathrm{eff}} = \varepsilon_r$ in this case.

Since $\rho_j^* = \rho_j + \rho_j^{\mathrm{dress}}$ we can write

$$\boldsymbol{\mu}_j^*(\boldsymbol{\omega}) = \int d\mathbf{r}\,\mathbf{r}\rho_j(\mathbf{r},\boldsymbol{\omega}) + \int d\mathbf{r}\,\mathbf{r}\rho_j^{\mathrm{dress}}(\mathbf{r},\boldsymbol{\omega}) = \boldsymbol{\mu}_j(\boldsymbol{\omega}) + \boldsymbol{\mu}_j^{\mathrm{dress}}(\boldsymbol{\omega})$$

and hence

$$\varepsilon_r = 1 + \frac{\beta}{3\varepsilon_0}\left[\sum_j n_j^{\mathrm{b}}\mu_j^2 + \sum_j n_j^{\mathrm{b}}\boldsymbol{\mu}_j \cdot \boldsymbol{\mu}_j^{\mathrm{dress}}\right] \quad \text{(nonelectrolyte)}, \tag{78}$$

where $\mu_j = |\boldsymbol{\mu}_j|$. The first term in the square bracket is a dipolar "self-term" and the second term is the contribution from intermolecular correlations.

For an electrolyte, b_0^* and hence $\mathcal{E}_r^*$ and $\mathcal{E}_r^{\mathrm{eff}}$ contain the same dipolar term as a nonelectrolyte (the value of the term is, however, different), but the second moment terms in Eq. (74) contribute as well. Since $\kappa \neq 0$ the higher order terms in Eqs. (75) and (76) also contribute, but let us focus on b_0^* to start with. The remaining terms are treated in Section III E.

It is of particular interest to consider contributions to $\mathcal{E}_r^*$ from ion pairs. The ions in an ion pair belong to two separate species, but if the pairs are held strongly together it would be a good approximation to consider them as a separate additional species. The fraction of ions that remain unpaired should, of course, still be treated as belonging to the ionic species. As an example we take a symmetric electrolyte with spherical ions of density $n^{\mathrm{b}} = n_+^{\mathrm{b}} = n_-^{\mathrm{b}}$. If a fraction ξ of the ions are involved in ion pairing, the ions pairs considered as an electroneutral species would have number density $n_{\mathrm{pair}}^{\mathrm{b}} = \xi n^{\mathrm{b}}$. The dipolar self-term from this species equals $\beta n_{\mathrm{pair}}^{\mathrm{b}}(\mu^{\mathrm{pair}})^2/(3\varepsilon_0)$ [cf. Eq. (78)], where μ^{pair} is the dipole moment of the pair. Let us compare this with the result we obtained in the discussion of ion pairing in section II C, where we did not distinguish paired and unpaired ions. The ion pairs then gave a contribution to $\mathcal{E}_r^*$ equal to $\xi\beta n^{\mathrm{b}}(\mu^{\mathrm{pair}})^2/(3\varepsilon_0)$, which originates from the second-moment term containing $q_l m_l^{*(2)}$ in Eq. (51) [here this term is included in b_0, see Eq. (74)]. This result is the same as that from the dipolar self-term since $\xi n^{\mathrm{b}} = n_{\mathrm{pair}}^{\mathrm{b}}$. Thus ion pairs treated as separate ions contribute in the same way as pairs treated as dipolar molecules. In addition there are, of course, further contributions from intermolecular correlations. For instance, the dipole-dipole correlations between ion pairs correspond to contributions to the four-particle correlations between the separate ions. All such effects are implicitly contained in ρ_j^* for all j in an exact theory.

In general, a particularly strong association of ions into pairs can, for example, be due to short-ranged interactions like hydrogen bonding or due to an unsymmetric charge distribution with a patch of negative charge on the surface of one species and a patch of positive charge on the other. These cases are all included in the present formalism. Extensive ion pairing would make ion pairs in the ionic liquid to function like a dipolar solvent for the remaining unassociated ions. Then κ can be real valued and small, so the screened electrostatics would be similar to electrolyte solutions at small to moderate concentrations. It must be stressed, however, that *actual ion pairing is not a necessity for this to happen.* Strong attractions between anions and cations can be an effect of many-body ion-ion correlations and transient association complexes can be quite different from ion pairs. In general, association should be interpreted in terms of how the ions correlate to each other rather than in terms of well defined long-lived complexes. The latter may, however, exist in particular cases.

In exactly the same manner as argued at the end of Section II C, one can show that the decay parameter κ is small and hence the decay length λ large if the values of the dressed ion charges q_j^* for all j are small, irrespectively of the reason for this. Small q_j^* values and a large value of $b_0^* = \tilde{\epsilon}_{\mathrm{reg}}(0)$ both favor a large decay length. Both in a dilute electrolyte solution and an ionic liquid with $\kappa \approx 0$ we have $\mathcal{E}_r^* \approx \tilde{\epsilon}_{\mathrm{reg}}(0)$. In the former case we have $\tilde{\epsilon}_{\mathrm{reg}}(0) \approx \varepsilon_r$, i.e., the dielectric constant of the solvent, while in the latter case the quantity $\tilde{\epsilon}_{\mathrm{reg}}(0)$ is something quite different since it originates from the ions and includes contributions from the last two terms in the square bracket in Eq. (74). Furthermore, in a dilute electrolyte solution $q_j^* \approx q_j$ for all j, while in the ionic liquids that we are considering here $q_j^* \approx 0$. The decay length λ is large in the former case since n_j^{b} for all ionic species are small (and possibly ε_r large), while in the letter case λ is large since q_j^* for all j are small (and possibly $\mathcal{E}_r^*$ large). Let us now return to the general case.

D. Anisotropy of the screened interactions and influences on the dielectric behavior

As a preparation for a further exploration of the screening behavior of ionic liquids, in particular the properties of the relative permittivity $\mathcal{E}_r^*$ and the decay parameter κ, it is useful to write the expression (70) for $\mathcal{E}_r^*$ and the equation for κ in yet another manner. The original equation (39) for κ can be written as

$$-\varepsilon_0 \kappa^2 = \int d\mathbf{r}'' e^{\kappa \hat{\mathbf{s}} \cdot \mathbf{r}''} \chi^*(r''),$$

where $\hat{\mathbf{s}}$ is an arbitrary unit vector. By inserting Eq. (64), setting $\mathbf{r}'' = \mathbf{r}_{42} = \mathbf{r}_{32} - \mathbf{r}_{34}$ and realizing that any two of $\mathbf{r}_2$, $\mathbf{r}_3$ and $\mathbf{r}_4$ can be selected as independent variables in the integrations for a bulk liquid we obtain

$$\begin{aligned}\varepsilon_0\kappa^2 &= \beta\sum_j \int d\boldsymbol{\omega}_3 \int d\mathbf{r}_2 d\mathbf{r}_4 e^{\kappa\hat{\mathbf{s}}\cdot(\mathbf{r}_{32}-\mathbf{r}_{34})} n_j^{\mathrm{b}} \rho_j^*(\mathbf{r}_{34},\boldsymbol{\omega}_3)\sigma_j(\mathbf{r}_{32},\boldsymbol{\omega}_3)\\ &= \beta\sum_j n_j^{\mathrm{b}} \int d\boldsymbol{\omega}_3 \int d\mathbf{r}_{32} e^{\kappa\hat{\mathbf{s}}\cdot\mathbf{r}_{32}}\sigma_j(\mathbf{r}_{32},\boldsymbol{\omega}_3) \int d\mathbf{r}_{34} e^{-\kappa\hat{\mathbf{s}}\cdot\mathbf{r}_{34}}\rho_j^*(\mathbf{r}_{34},\boldsymbol{\omega}_3).\end{aligned}$$

This can be expressed as

$$\kappa^2 = \frac{\beta}{\varepsilon_0}\sum_j n_j^{\mathrm{b}} \left\langle \mathrm{Q}_j(\hat{\mathbf{s}},\boldsymbol{\omega}_3)\mathrm{Q}_j^{\mathrm{eff}}(-\hat{\mathbf{s}},\boldsymbol{\omega}_3)\right\rangle_{\boldsymbol{\omega}_3}, \tag{79}$$

where we have defined

$$\mathrm{Q}_j(\hat{\mathbf{r}},\boldsymbol{\omega}) = \int d\mathbf{r}'\sigma_j(\mathbf{r}',\boldsymbol{\omega})e^{\kappa\hat{\mathbf{r}}\cdot\mathbf{r}'} \tag{80}$$

$$\mathrm{Q}_j^{\mathrm{eff}}(\hat{\mathbf{r}},\boldsymbol{\omega}) = \int d\mathbf{r}'\rho_j^*(\mathbf{r}',\boldsymbol{\omega})e^{\kappa\hat{\mathbf{r}}\cdot\mathbf{r}'}. \tag{81}$$

Since the average over the orientations is taken in Eq. (79), the rhs is independent of $\hat{\mathbf{s}}$.

Furthermore, Eq. (70) can be written in terms of Q_j and $\mathrm{Q}_j^{\mathrm{eff}}$

$$\mathcal{E}_r^* = 1 - \frac{\beta}{\varepsilon_0\kappa^2}\sum_j n_j^{\mathrm{b}}\left\langle \mathrm{Q}_j^{\mathrm{eff}}(-\hat{\mathbf{k}},\boldsymbol{\omega})\mathrm{Q}_j(\hat{\mathbf{k}},\boldsymbol{\omega}) - q_j^* q_j\right\rangle_{\boldsymbol{\omega}}, \tag{82}$$

where we have made the identification

$$\tilde{\rho}_j^*(\mathrm{i}\kappa\hat{\mathbf{k}},\boldsymbol{\omega}) = \int d\mathbf{r}\rho_j^*(\mathbf{r},\boldsymbol{\omega})e^{\kappa\hat{\mathbf{k}}\cdot\mathbf{r}} \equiv \mathrm{Q}_j^{\mathrm{eff}}(\hat{\mathbf{k}},\boldsymbol{\omega}) \tag{83}$$

and likewise for $\tilde{\sigma}_j$. The first equality in Eq. (83) follows from the definition of the Fourier transform; the resulting integral is a kind of Laplace transform, cf. Eq. (42). (For completeness we note that Eq. (79) can alternatively be obtained from $\tilde{\epsilon}(\mathrm{i}\kappa) = 0$ by inserting $k = \mathrm{i}\kappa$ and $\mathbf{k} = k\hat{\mathbf{k}}$ in Eq. (69), using Eq. (83) and replacing $\hat{\mathbf{k}}$ by $\hat{\mathbf{s}}$.)

$\mathrm{Q}_j^{\mathrm{eff}}$ is, in fact, an entity that gives the magnitude of the electrostatic potential from a j ion for large distances[38]

$$\psi_j(\mathbf{r},\boldsymbol{\omega}) \sim \mathrm{Q}_j^{\mathrm{eff}}(\hat{\mathbf{r}},\boldsymbol{\omega})\phi_{\mathrm{Coul}}^*(r), \quad r\to\infty. \tag{84}$$

which implies that the leading term decays as $\psi_j(\mathbf{r},\boldsymbol{\omega}) \sim \mathrm{Q}_j^{\mathrm{eff}}(\hat{\mathbf{r}},\boldsymbol{\omega})\exp(-\kappa r)/(4\pi\mathcal{E}_r^{\mathrm{eff}}\varepsilon_0 r)$. Likewise, Q_j gives the magnitude of the screened potential from the internal charge density σ_j (i.e., without any contribution from the ion cloud)

$$\psi_j^{\sigma}(\mathbf{r},\boldsymbol{\omega}) \sim \mathrm{Q}_j(\hat{\mathbf{r}},\boldsymbol{\omega})\phi_{\mathrm{Coul}}^*(r), \quad r\to\infty \tag{85}$$

where ψ_j^σ is defined as

$$\psi_j^\sigma(\mathbf{r},\boldsymbol{\omega}) \equiv \int d\mathbf{r}'\sigma_j(\mathbf{r}',\boldsymbol{\omega})\phi^*_{\mathrm{Coul}}(|\mathbf{r}-\mathbf{r}'|).$$

This can be easily realized from the fact that

$$\int d\mathbf{r}'\sigma_j(\mathbf{r}',\boldsymbol{\omega})\phi^*_{\mathrm{Coul}}(|\mathbf{r}-\mathbf{r}'|) \sim \int d\mathbf{r}'\sigma_j(\mathbf{r}',\boldsymbol{\omega})\frac{e^{-\kappa|\mathbf{r}-\mathbf{r}'|}}{4\pi\mathcal{E}_r^{\mathrm{eff}}\varepsilon_0|\mathbf{r}-\mathbf{r}'|}$$

when $r\to\infty$. Since

$$\frac{e^{-\kappa|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \sim \frac{e^{-\kappa(r-\hat{\mathbf{r}}\cdot\mathbf{r}')}}{r} = \frac{e^{-\kappa r}}{r}e^{\kappa\hat{\mathbf{r}}\cdot\mathbf{r}'} \quad \text{when } r'\ll r\to\infty,$$

where $\hat{\mathbf{r}}=\mathbf{r}/r$, it follows that

$$\psi_j^\sigma(\mathbf{r},\boldsymbol{\omega}) \sim \int d\mathbf{r}'\sigma_j(\mathbf{r}',\boldsymbol{\omega})e^{\kappa\hat{\mathbf{r}}\cdot\mathbf{r}'}\frac{e^{-\kappa r}}{4\pi\mathcal{E}_r^{\mathrm{eff}}\varepsilon_0 r}, \quad r\to\infty,$$

which is the same as Eq. (85). Eq. (84) can be derived from Eq. (67) in the same manner.

The dependence of $\mathsf{Q}_j^{\mathrm{eff}}(\hat{\mathbf{r}},\boldsymbol{\omega})$ on $\hat{\mathbf{r}}$ shows how the potential $\psi_j(\hat{\mathbf{r}},\boldsymbol{\omega})$ from an ion varies in different directions – a behavior that distinguishes an electrolyte from a nonelectrolyte; for the latter the potential far away from a charge distribution is independent of the direction and is proportional to the total charge of the distribution. The fact that the direction dependence of the electrostatic potential persists when $r\to\infty$ in an electrolyte, which incidentally is also valid in the PB approximation,[64–67] has important consequences, see for example Ref. [65]. The leading term for the potential of mean force is given by

$$w_{ij}(\mathbf{r}_{12},\boldsymbol{\omega}_1,\boldsymbol{\omega}_2) \sim \mathsf{Q}_i^{\mathrm{eff}}(\hat{\mathbf{r}}_{12},\boldsymbol{\omega}_1)\mathsf{Q}_j^{\mathrm{eff}}(-\hat{\mathbf{r}}_{12},\boldsymbol{\omega}_2)\frac{e^{-\kappa r_{12}}}{4\pi\mathcal{E}_r^{\mathrm{eff}}\varepsilon_0 r_{12}}, \quad r_{12}\to\infty \tag{86}$$

Note that the vector $\hat{\mathbf{r}}_{12}$ in $\mathsf{Q}_i^{\mathrm{eff}}$ for the i molecule located at $\mathbf{r}_1$ points towards the j molecule located at $\mathbf{r}_2$, while $-\hat{\mathbf{r}}_{12}$ in $\mathsf{Q}_j^{\mathrm{eff}}$ for the j molecule points towards the i molecule.

The direction independent (isotropic) parts of $\psi_j^\sigma(\mathbf{r},\boldsymbol{\omega})$ and $\psi_j(\hat{\mathbf{r}},\boldsymbol{\omega})$ can be obtained by taking the average over all directions $\hat{\mathbf{r}}$. For ψ_j^σ we have

$$\left\langle\psi_j^\sigma(\mathbf{r},\boldsymbol{\omega})\right\rangle_{\hat{\mathbf{r}}} \sim \left\langle\mathsf{Q}_j(\hat{\mathbf{r}},\boldsymbol{\omega})\right\rangle_{\hat{\mathbf{r}}}\phi^*_{\mathrm{Coul}}(r) = \mathcal{Q}_j\phi^*_{\mathrm{Coul}}(r), \quad r\to\infty,$$

where (distinguish $\mathcal{Q}_j$ from Q_j)

$$\begin{aligned}\mathcal{Q}_j &= \int d\mathbf{r}'\sigma_j(\mathbf{r}',\boldsymbol{\omega})\left\langle e^{\kappa\hat{\mathbf{r}}\cdot\mathbf{r}'}\right\rangle_{\hat{\mathbf{r}}} = \int d\mathbf{r}'\sigma_j(\mathbf{r}',\boldsymbol{\omega})\frac{1}{4\pi}\int d\hat{\mathbf{r}}\, e^{\kappa\hat{\mathbf{r}}\cdot\mathbf{r}'} \\ &= \int d\mathbf{r}'\sigma_j(\mathbf{r}',\boldsymbol{\omega})\frac{\sinh(\kappa r')}{\kappa r'}\end{aligned} \tag{87}$$

is independent of the orientation $\boldsymbol{\omega}$ (in the integration $\hat{\mathbf{r}}$ represents the polar coordinate angles). Note that $\mathcal{Q}_j$ is in general different from the charge q_j of the ion defined in Eq. (52). Likewise, we obtain the direction independent part of $\psi_j(\hat{\mathbf{r}}, \boldsymbol{\omega})$ as $\mathcal{Q}_j^{\text{eff}} \phi^*_{\text{Coul}}(r)$ where

$$\mathcal{Q}_j^{\text{eff}} = \int d\mathbf{r}' \rho_j^*(\mathbf{r}', \boldsymbol{\omega}) \frac{\sinh(\kappa r')}{\kappa r'} \tag{88}$$

defines the effective charge for a j ion.

The anisotropy of the potentials ψ_j^σ and ψ_j expressed by the $\hat{\mathbf{r}}$ dependence of $\mathsf{Q}_j(\hat{\mathbf{r}}, \boldsymbol{\omega})$ and $\mathsf{Q}_j^{\text{eff}}(\hat{\mathbf{r}}, \boldsymbol{\omega})$, respectively, can be expressed in terms of a kind of multipole expansion. For the former we have[38]

$$\mathsf{Q}_j(\hat{\mathbf{r}}, \boldsymbol{\omega}) = \mathcal{Q}_j + \kappa \boldsymbol{\mathcal{Q}}_j^{(1)}(\boldsymbol{\omega}) \cdot \hat{\mathbf{r}} + \frac{\kappa^2}{3} \hat{\mathbf{r}} \cdot \boldsymbol{\mathcal{Q}}_j^{(2)}(\boldsymbol{\omega}) \cdot \hat{\mathbf{r}} + \dots \tag{89}$$

where

$$\boldsymbol{\mathcal{Q}}_j^{(l)}(\boldsymbol{\omega}) = (2l+1)!! \int d\mathbf{r}' \, \mathbf{P}_l(\mathbf{r}') \sigma_j(\mathbf{r}', \boldsymbol{\omega}) \frac{i_l(\kappa r')}{(\kappa r')^l} \tag{90}$$

for $l \geq 0$ constitute generalized multipole moments, $(2l+1)!! = (2l+1)(2l-1)\cdot \ldots \cdot 3 \cdot 1$ and $i_l(x)$ is a modified spherical Bessel function $[i_l(x) = j_l(\mathrm{i}x)/\mathrm{i}^l$, where $j_l(x)$ is an ordinary spherical Bessel function]. In the limit $\kappa \to 0$ these moments reduce to the ordinary ones, $\boldsymbol{\mathcal{M}}_j^{(l)}(\boldsymbol{\omega})$, defined in Eq. (55) since $i_l(x)/x^l \to 1/(2l+1)!!$ when $x \to 0$. Note that $i_0(x) = \sinh(x)/x$ and $\mathbf{P}_0 = 1$, so Eq. (87) can also be written as in Eq. (90) with $\boldsymbol{\mathcal{Q}}_j^{(0)} = \mathcal{Q}_j$.

When the decay length $1/\kappa$ is significantly larger than the molecular size, the generalized multipole moments $\boldsymbol{\mathcal{Q}}_j^{(l)}$ are virtually equal to the ordinary ones, $\boldsymbol{\mathcal{M}}_j^{(l)}$. This can be seen from Eq. (90) since under these circumstances $i_l(\kappa r')/(\kappa r')^l \approx 1/(2l+1)!!$ inside the molecule (where $\sigma_i \neq 0$), which implies that $\boldsymbol{\mathcal{Q}}_j^{(l)}(\boldsymbol{\omega}) \approx \boldsymbol{\mathcal{M}}_j^{(l)}(\boldsymbol{\omega})$; for example, $\mathcal{Q}_j \approx q_j$ and $\boldsymbol{\mathcal{Q}}_j^{(1)}(\boldsymbol{\omega}) \approx \boldsymbol{\mu}_j(\boldsymbol{\omega})$. Furthermore, for large decay lengths (small κ), the multipolar terms in the expansion (89) are in general not very important since they have the factor κ^l in front of them.

Likewise, we have

$$\begin{aligned}\mathsf{Q}_j^{\text{eff}}(\hat{\mathbf{r}}, \boldsymbol{\omega}) &= \mathcal{Q}_j^{\text{eff}} + \kappa \boldsymbol{\mathcal{Q}}_j^{\text{eff}(1)}(\boldsymbol{\omega}) \cdot \hat{\mathbf{r}} + \frac{\kappa^2}{3} \hat{\mathbf{r}} \cdot \boldsymbol{\mathcal{Q}}_j^{\text{eff}(2)}(\boldsymbol{\omega}) \cdot \hat{\mathbf{r}} + \dots \\ &\equiv \mathcal{Q}_j^{\text{eff}} + \kappa \boldsymbol{\mu}_j^{\text{eff}}(\boldsymbol{\omega}) \cdot \hat{\mathbf{r}} + \frac{\kappa^2}{3} \hat{\mathbf{r}} \cdot \boldsymbol{\Theta}_j^{\text{eff}}(\boldsymbol{\omega}) \cdot \hat{\mathbf{r}} + \dots ,\end{aligned} \tag{91}$$

where

$$\boldsymbol{\mathcal{Q}}_j^{\text{eff}(l)}(\boldsymbol{\omega}) = (2l+1)!! \int d\mathbf{r} \, \mathbf{P}_l(\mathbf{r}') \rho_j^*(\mathbf{r}', \boldsymbol{\omega}) \frac{i_l(\kappa r')}{(\kappa r')^l}, \tag{92}$$

and where we in the second line have used the alternative notations for the first few moments

$$\boldsymbol{\mu}_j^{\mathrm{eff}} = \boldsymbol{\mathcal{Q}}_j^{\mathrm{eff}(1)} \text{ and } \boldsymbol{\Theta}_j^{\mathrm{eff}} = \boldsymbol{\mathcal{Q}}_j^{\mathrm{eff}(2)}. \tag{93}$$

Note, however, that the expansion for Q_j in Eq. (89) cannot be written in a similar manner with q_j, $\boldsymbol{\mu}_j$ and $\boldsymbol{\Theta}_j$ since we have in general $\mathcal{Q}_j \neq q_j$, $\boldsymbol{\mathcal{Q}}_j^{(1)} \neq \boldsymbol{\mu}_j$ and $\boldsymbol{\mathcal{Q}}_j^{(2)} \neq \boldsymbol{\Theta}_j$. The latter are equal only when $\kappa = 0$.

The expansions for $\mathsf{Q}_j(\hat{\mathbf{r}}, \boldsymbol{\omega})$ and $\mathsf{Q}_j^{\mathrm{eff}}(\hat{\mathbf{r}}, \boldsymbol{\omega})$ in Eqs. (89) and (91) can be inserted in Eq. (82) in order to obtain the higher multipole moment contributions to $\mathcal{E}_r^*$. The resulting expression is Eq. (B18), which is derived in Appendix B. This is the starting point of the discussion of $\mathcal{E}_r^*$ in the next section, see Eq. (97).

For completeness we note that the entire expression for the decay of ψ_j^σ when $r \to \infty$ is[38]

$$\psi_j^\sigma(\mathbf{r}, \boldsymbol{\omega}) \sim \frac{1}{4\pi \mathcal{E}_r^{\mathrm{eff}} \varepsilon_0} \left[\mathsf{Q}_j(\hat{\mathbf{r}}, \boldsymbol{\omega}) \frac{e^{-\kappa r}}{r} + \mathsf{Q}_j'(\hat{\mathbf{r}}, \boldsymbol{\omega}) \frac{e^{-\kappa r}}{r^2} + \mathsf{Q}_j''(\hat{\mathbf{r}}, \boldsymbol{\omega}) \frac{e^{-\kappa r}}{r^3} + \ldots \right],$$

where $\mathsf{Q}_j'(\hat{\mathbf{r}}, \boldsymbol{\omega}) = \boldsymbol{\mathcal{Q}}_j^{(1)}(\boldsymbol{\omega}) \cdot \hat{\mathbf{r}} + \kappa\, \hat{\mathbf{r}} \cdot \boldsymbol{\mathcal{Q}}_j^{(2)}(\boldsymbol{\omega}) \cdot \hat{\mathbf{r}} + \ldots$ starts with a dipolar term and $\mathsf{Q}_j''(\hat{\mathbf{r}}, \boldsymbol{\omega}) = \hat{\mathbf{r}} \cdot \boldsymbol{\mathcal{Q}}_j^{(2)}(\boldsymbol{\omega}) \cdot \hat{\mathbf{r}} + \ldots$ starts with a quadrupolar term. Thus, when $\kappa \to 0$ we recover the usual multipole expansion for the potential containing $q_j/r + \boldsymbol{\mu}_j(\boldsymbol{\omega}) \cdot \hat{\mathbf{r}}/r^2 + \hat{\mathbf{r}} \cdot \boldsymbol{\Theta}_j(\boldsymbol{\omega}) \cdot \hat{\mathbf{r}}/r^3 + \ldots$. Analogous expressions apply[38] to ψ_j and $\mathsf{Q}_j^{\mathrm{eff}}$.

Eq. (84) is valid also when the decay parameter is complex, $\kappa = \kappa_{\Re} \pm \mathrm{i}\kappa_{\Im}$, provided one adds the contributions to ψ_i from each of these two κ values as explained earlier. We have

$$\psi_j(\mathbf{r}, \boldsymbol{\omega}) \sim \mathsf{Q}_j^{\mathrm{eff}}(\hat{\mathbf{r}}, \boldsymbol{\omega}) \frac{e^{-(\kappa_{\Re} + \mathrm{i}\kappa_{\Im})r}}{4\pi \mathsf{E}_r^{\mathrm{eff}} e^{\mathrm{i}\vartheta_{\mathsf{E}}} \varepsilon_0 r} + \underline{\mathsf{Q}}_j^{\mathrm{eff}}(\hat{\mathbf{r}}, \boldsymbol{\omega}) \frac{e^{-(\kappa_{\Re} - \mathrm{i}\kappa_{\Im})r}}{4\pi \mathsf{E}_r^{\mathrm{eff}} e^{-\mathrm{i}\vartheta_{\mathsf{E}}} \varepsilon_0 r}, \quad r \to \infty, \tag{94}$$

where

$$\mathsf{Q}_j^{\mathrm{eff}}(\hat{\mathbf{r}}, \boldsymbol{\omega}) = \int d\mathbf{r}' \rho_j^*(\mathbf{r}', \boldsymbol{\omega}) e^{(\kappa_{\Re} + \mathrm{i}\kappa_{\Im})\hat{\mathbf{r}} \cdot \mathbf{r}'}$$

now is complex valued and the underscore denotes complex conjugation. Writing $\mathsf{Q}_j^{\mathrm{eff}}(\hat{\mathbf{r}}, \boldsymbol{\omega}) = |\mathsf{Q}_j^{\mathrm{eff}}(\hat{\mathbf{r}}, \boldsymbol{\omega})| e^{-\mathrm{i}\gamma_j(\hat{\mathbf{r}}, \boldsymbol{\omega})}$ with a real-valued γ_j, we obtain from Eq. (94)

$$\psi_j(\mathbf{r}, \boldsymbol{\omega}) \sim |\mathsf{Q}_j^{\mathrm{eff}}(\hat{\mathbf{r}}, \boldsymbol{\omega})| \frac{e^{-\kappa_{\Re} r}}{2\pi \mathsf{E}_r^{\mathrm{eff}} \varepsilon_0 r} \cos[\kappa_{\Im} r + \vartheta_{\mathsf{E}} + \gamma_j(\hat{\mathbf{r}}, \boldsymbol{\omega})], \quad r \to \infty, \tag{95}$$

where both the magnitude and the phase of the oscillatory decay depend on the direction $\hat{\mathbf{r}}$. Likewise, for w_{ij} we obtain in an analogous manner

$$\begin{aligned} w_{ij}(\mathbf{r}_{12}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2) \sim\ & |\mathsf{Q}_i^{\mathrm{eff}}(\hat{\mathbf{r}}_{12}, \boldsymbol{\omega}_1) \mathsf{Q}_j^{\mathrm{eff}}(-\hat{\mathbf{r}}_{12}, \boldsymbol{\omega}_2)| \frac{e^{-\kappa_{\Re} r_{12}}}{2\pi \mathsf{E}_r^{\mathrm{eff}} \varepsilon_0 r} \\ & \times \cos[\kappa_{\Im} r_{12} + \vartheta_{\mathsf{E}} + \gamma_i(\hat{\mathbf{r}}_{12}, \boldsymbol{\omega}_1) + \gamma_j(-\hat{\mathbf{r}}_{12}, \boldsymbol{\omega}_2)], \quad r_{12} \to \infty. \end{aligned} \tag{96}$$

$\mathsf{Q}_i^{\mathrm{eff}}(\hat{\mathbf{r}}, \boldsymbol{\omega})$ can also in this case be written as a multipole expansion, similar to the one above.

E. The multipolar contributions to $\mathcal{E}_r^*$ and $\tilde{\epsilon}(k)$

We have seen that $\mathcal{E}_r^*$ contains the contributions included in the dielectric constant ε_r for non-electrolytes, as given by Eq. (77), but that there are additional important terms in electrolytes. In particular we have seen in Section III C how second moment terms ensures that the emergence of transitional electroneutral entities like ion pairs, give rise to effects like those from an actual electroneutral polar species present in the system. As noted above, since $\kappa \neq 0$ for an electrolyte, the higher order terms in Eq. (75), i.e., $-b_2^*\kappa^2$ etc., also contribute to $\mathcal{E}_r^*$ for electrolytes. While the dipolar contribution $\boldsymbol{\mu}_j \cdot \boldsymbol{\mu}_j^*$ is contained in b_0, the corresponding quadrupolar term is contained in b_2^*. As can be seen in Eq. (B22), b_2^* contains the product $\boldsymbol{\Theta}_j \bullet \boldsymbol{\Theta}_j^*$, where $\boldsymbol{\Theta}_j^*$ is the quadrupole moment of the charge distributions ρ_j^* and the symbol $\bullet$ denotes a product of quadrupole moment components defined from $\boldsymbol{\Theta}_j \bullet \boldsymbol{\Theta}_j^* = \sum_{\alpha,\alpha'} \Theta_{j;\alpha\alpha'} \Theta_{j;\alpha\alpha'}^*$, where α and α' run over x, y, z (in general, the $\bullet$ symbol denotes the full contraction product of the tensors, see Appendix B). The corresponding octupolar contributions to $\mathcal{E}_r^*$ are contained in $b_4^*\kappa^4$ and the hexadecapolar ones in $-b_6^*\kappa^6$ (not shown in Eq. (75), but see Eq. (B24)). In addition there are various other kinds of moments contributing like $\boldsymbol{\mu}_j \cdot \int d\mathbf{r}\, \mathbf{r}\, r^2 \rho_j^*(\mathbf{r}, \boldsymbol{\omega})$ as shown in Eq. (B22). These kinds of rather complicated contributions are unavoidable in Taylor expansions of $\tilde{\epsilon}_{\mathrm{reg}}(k)$ and $\mathcal{E}_r^* = \tilde{\epsilon}_{\mathrm{reg}}(\mathrm{i}\kappa)$ and the expressions become increasingly more intricate for the higher moment terms. We will therefore utilize a different expansion.

A more straightforward manner to write a multipolar expansion of $\mathcal{E}_r^*$ is obtained in Appendix B from the expansion of $\tilde{\epsilon}_{\mathrm{reg}}(k)$ in Eq. (B17). The expression for $\mathcal{E}_r^*$ is given in Eq. (B18), which can be written

$$\mathcal{E}_r^* = 1 - \frac{\beta}{\varepsilon_0} \sum_j n_j^{\mathrm{b}} \left[\frac{d_j^{(0)}}{\kappa^2} + d_j^{(1)} + d_j^{(2)}\kappa^2 + d_j^{(3)}\kappa^4 + \dots \right], \tag{97}$$

where

$$\begin{aligned} d_j^{(0)} &= \mathcal{Q}_j \mathcal{Q}_j^{\mathrm{eff}} - q_j q_j^*, \\ d_j^{(1)} &= -\frac{1}{3} \boldsymbol{\mathcal{Q}}_j^{(1)} \cdot \boldsymbol{\mathcal{Q}}_j^{\mathrm{eff}(1)}, \\ d_j^{(2)} &= \frac{2}{135} \boldsymbol{\mathcal{Q}}_j^{(2)} \bullet \boldsymbol{\mathcal{Q}}_j^{\mathrm{eff}(2)} \end{aligned}$$

and

$$d_j^{(3)} = -\frac{2}{7875} \boldsymbol{\mathcal{Q}}_j^{(3)} \bullet \boldsymbol{\mathcal{Q}}_j^{\mathrm{eff}(3)}.$$

In general

$$d_j^{(l)} = \frac{(-1)^l (2l+1)^2\, l!}{[(2l+1)!!]^3} \boldsymbol{\mathcal{Q}}_j^{(l)} \bullet \boldsymbol{\mathcal{Q}}_j^{\mathrm{eff}(l)}.$$

The product $\boldsymbol{\mathcal{Q}}_j^{(l)} \bullet \boldsymbol{\mathcal{Q}}_j^{\mathrm{eff}(l)}$ is independent of ω. By using the notation in Eq. (93) we can alternatively write the second and third coefficients as

$$d_j^{(1)} = -\frac{1}{3} \boldsymbol{\mathcal{Q}}_j^{(1)} \cdot \boldsymbol{\mu}_j^{\mathrm{eff}},$$
$$d_j^{(2)} = \frac{2}{135} \boldsymbol{\mathcal{Q}}_j^{(2)} \bullet \boldsymbol{\Theta}_j^{\mathrm{eff}}.$$

In contrast to Eq. (73), Eq. (97) is not a Taylor expansion in κ since $d_j^{(l)}$ depends on κ, but these coefficients are much simpler than in Eq. (73) since they only contain generalized multipole moments. The other moments (second, fourth moments etc. of various kinds) in the b_ν^* coefficients originate from the κ dependence of $\boldsymbol{\mathcal{Q}}_j^{(l)}$ and $\boldsymbol{\mathcal{Q}}_j^{\mathrm{eff}(l)}$ in $d_j^{(l)}$. A major point of the Taylor expansion (73) is, however, to make the connection to the nonelectrolyte case clear as explained in Section III C.

Both Eqs. (82) and (97) are expressions of $\mathcal{E}_r^*$ in terms of the coefficients for the long-range decay of the potentials ψ_i^σ and ψ_i. In the latter equation we see that the generalized multipole moments of various orders occur in separate terms. When κ is small and hence the decay length is large, the higher order terms in Eq. (97) are not very important. Note that $d_j^{(0)}$ goes to zero proportionally to κ^2 when $\kappa \to 0$, so $d_j^{(0)}/\kappa^2$ stays finite (this term gives the second moment contributions to b_0^* in this limit). Explicitly, we can write this term as

$$\begin{aligned}
\frac{d_j^{(0)}}{\kappa^2} &= \frac{\mathcal{Q}_j \mathcal{Q}_j^{\mathrm{eff}} - q_j q_j^*}{\kappa^2} = \frac{\mathcal{Q}_j^{\mathrm{eff}} \left[\mathcal{Q}_j - q_j\right] + q_j \left[\mathcal{Q}_j^{\mathrm{eff}} - q_j^*\right]}{\kappa^2} \\
&= \mathcal{Q}_j^{\mathrm{eff}} \int d\mathbf{r}\, r^2\, \sigma_j(\mathbf{r}, \boldsymbol{\omega}) \frac{\sinh(\kappa r) - \kappa r}{(\kappa r)^3} \\
&\quad + q_j \int d\mathbf{r}\, r^2\, \rho_j^*(\mathbf{r}, \boldsymbol{\omega}) \frac{\sinh(\kappa r) - \kappa r}{(\kappa r)^3}.
\end{aligned} \tag{98}$$

The last term contains the same integral as in the expression for $\mathcal{E}_r^*$ for spherical ions, Eq. (49). In the latter case, the second last term is zero since there is only a point change at the center of the ion and $\mathcal{Q}_j = q_j$. Furthermore, due to the spherical symmetry the dipolar and all multipolar terms in Eq. (97) are zero, so this equation reduces to Eq. (49).

As noted earlier, when the decay length $1/\kappa$ is significantly larger than the molecular size we have $\boldsymbol{\mathcal{Q}}_j^{(l)}(\boldsymbol{\omega}) \approx \boldsymbol{\mathcal{M}}_j^{(l)}(\boldsymbol{\omega})$ and then we can write as a good approximation

$$d_j^{(1)} \approx -\frac{1}{3} \boldsymbol{\mu}_j \cdot \boldsymbol{\mu}_j^{\mathrm{eff}},$$
$$d_j^{(2)} \approx \frac{2}{135} \boldsymbol{\Theta}_j \bullet \boldsymbol{\Theta}_j^{\mathrm{eff}}.$$

$$d_j^{(3)} \approx \frac{2}{7875}\boldsymbol{\mathcal{M}}_j^{(3)} \bullet \boldsymbol{\mathcal{Q}}_j^{\mathrm{eff}(3)},$$

which can be inserted in Eq. (97). Furthermore, we have in Eq. (98)

$$\int d\mathbf{r}\, r^2\, \sigma_j(\mathbf{r},\boldsymbol{\omega}) \left[\frac{\sinh(\kappa r)-\kappa r}{(\kappa r)^3}\right] \approx \frac{1}{6}\int d\mathbf{r}\, r^2\, \sigma_j(\mathbf{r},\boldsymbol{\omega}) = \frac{m_j^{(2)}}{6}$$

since the square bracket is virtually constant inside the molecule.

When κ is small, for instance when there is a large amount of ion pairing, a reasonable approximation would be to set $d_j^{(3)}\kappa^4 + \ldots \approx 0$ and obtain

$$\mathcal{E}_r^* \approx 1 - \frac{\beta}{\varepsilon_0}\sum_j n_j^{\mathrm{b}} \left[\frac{1}{6}m_j^{(2)}\mathcal{Q}_j^{\mathrm{eff}} + \frac{q_j(\mathcal{Q}_j^{\mathrm{eff}} - q_j^*)}{\kappa^2} - \frac{1}{3}\boldsymbol{\mu}_j\cdot\boldsymbol{\mu}_j^{\mathrm{eff}} + \frac{2\kappa^2}{135}\boldsymbol{\Theta}_j \bullet \boldsymbol{\Theta}_j^{\mathrm{eff}}\right]. \qquad (99)$$

The second term in the square bracket,

$$\frac{\mathcal{Q}_j^{\mathrm{eff}} - q_j^*}{\kappa^2} = \int d\mathbf{r}\, r^2\, \rho_j^*(\mathbf{r},\boldsymbol{\omega})\frac{\sinh(\kappa r)-\kappa r}{(\kappa r)^3}, \qquad (100)$$

contains contributions due to ion pairing as discussed in sections II C and III C. The third term corresponds to the dipolar contribution for nonelectrolytes, Eq. (77) [for nonelectrolytes $\boldsymbol{\mu}_j^{\mathrm{eff}} = \boldsymbol{\mu}_j^*$ since $\kappa = 0$]. The dipolar and quadrupolar contributions are, of course, also affected by ion pairing. All terms contain the effects of correlations (via $\mathcal{Q}_j^{\mathrm{eff}}$, q_j^*, $\boldsymbol{\mu}_j^{\mathrm{eff}}$ and $\boldsymbol{\Theta}_j^{\mathrm{eff}}$).

As we have seen in the previous section, in the limit $\kappa \to 0$ we have $\mathcal{E}_r^* \to b_0^* = \tilde{\epsilon}_{\mathrm{reg}}(0)$, which is also the limit of the rhs of Eq. (99) since $\mathcal{Q}_j^{\mathrm{eff}} \to q_j^*$, $\boldsymbol{\mu}_j^{\mathrm{eff}} \to \boldsymbol{\mu}_j^*$ and the integral in Eq. (100) goes to $m_j^{*(2)}/6$. Hence we have

$$\mathcal{E}_r^* \approx 1 - \frac{\beta}{\varepsilon_0}\sum_j n_j^{\mathrm{b}}\left[\frac{1}{6}\left(q_j^* m_j^{(2)} + q_j m_j^{*(2)}\right) - \frac{1}{3}\boldsymbol{\mu}_j\cdot\boldsymbol{\mu}_j^*\right] \qquad (101)$$

when κ in very small.

The presence of all contributions to $\mathcal{E}_r^*$ in Eq. (97) apart from the dipolar term in Eq. (101) (which constitute the only term in the dielectric constant ε_r for a pure polar liquid) implies that the meaning of polarity for ionic liquids as expressed by the permittivity is not the same as the polarity of polar liquids. For ionic liquids with small κ the difference is, however, less than for those with large κ since the higher multipolar contributions go to zero when $\kappa \to 0$. For ionic liquids the second moment terms in Eq. (101) remain even when κ is very small.

For completeness, we also give the expansion of $\tilde{\epsilon}(k)$ in multipolar terms, corresponding to Eq. (97). As shown in Appendix B, $\tilde{\epsilon}(k)$ in Eq. (69) can be written (cf. Eq (B16))

$$\tilde{\epsilon}(k) = 1 + \frac{\beta}{\varepsilon_0}\sum_j n_j^{\mathrm{b}}\left[\frac{D_j^{(0)}(k)}{k^2} + D_j^{(1)}(k) + D_j^{(2)}(k)k^2 + D_j^{(3)}(k)k^4 + \ldots\right], \qquad (102)$$

where the functions $D_j^{(l)}(k)$, expressed in terms of the cartesian multipolar tensors $\tilde{\boldsymbol{\rho}}_j^{*(l)}(k, \boldsymbol{\omega})$ and $\tilde{\boldsymbol{\sigma}}_j^{(l)}(k, \boldsymbol{\omega})$ [associated with $\tilde{\rho}_j^{*}(\mathbf{k}, \boldsymbol{\omega})$ of $\tilde{\sigma}_j(\mathbf{k}, \boldsymbol{\omega})$, and defined in Eqs. (B13) and (B14), respectively], are given by

$$\begin{aligned} D_j^{(0)}(k) &= \tilde{\rho}_j^{*(0)}(k)\tilde{\sigma}_j^{(0)}(k), \\ D_j^{(1)}(k) &= \frac{1}{3}\tilde{\boldsymbol{\rho}}_j^{*(1)}(k, \boldsymbol{\omega}) \cdot \tilde{\boldsymbol{\sigma}}_j^{(1)}(k, \boldsymbol{\omega}), \\ D_j^{(2)}(k) &= \frac{2}{135}\tilde{\boldsymbol{\rho}}_j^{*(2)}(k, \boldsymbol{\omega}) \bullet \tilde{\boldsymbol{\sigma}}_j^{(2)}(k, \boldsymbol{\omega}) \end{aligned}$$

and, in general,

$$D_j^{(l)}(k) = \frac{(2l+1)^2\, l!}{[(2l+1)!!]^3}\, \tilde{\boldsymbol{\rho}}_j^{*(l)}(k, \boldsymbol{\omega}) \bullet \tilde{\boldsymbol{\sigma}}_j^{(l)}(k, \boldsymbol{\omega}).$$

$D_j^{(0)}$ is the product of two scalars, $D_j^{(1)}$ is the dot product of two vectors (like dipoles) and $D_j^{(2)}$ is the full contraction product of two second order tensors (like quadrupoles), etc. Due to the dot and contraction products in the rhs, all $D_j^{(l)}(k)$ functions are independent of $\boldsymbol{\omega}$. Note that the expressions for $\tilde{\boldsymbol{\rho}}_j^{*(l)}$ and $\tilde{\boldsymbol{\sigma}}_j^{(l)}$ in Eqs. (B13) and (B14) evaluated at $k = i\kappa$ become equal to the generalized multipole moments $\boldsymbol{\mathcal{Q}}_j^{\mathrm{eff}(l)}$ and $\boldsymbol{\mathcal{Q}}_j^{(l)}$ in Eqs. (92) and (90), respectively. The multipolar expansion of $\tilde{\varepsilon}(k)$ in terms of the corresponding spherical tensors associated with $\tilde{\rho}_j^{*}(\mathbf{k}, \boldsymbol{\omega})$ and $\tilde{\sigma}_j(\mathbf{k}, \boldsymbol{\omega})$ is given in Eq. (B9). Likewise, $1/\tilde{\varepsilon}(k)$ can be expanded in similar manners, see Eqs. (B30) and (B31).

IV. SUMMARY AND CONCLUSIONS

In this paper we do an exact statistical mechanical analysis of electrostatic screening in and dielectric properties of ionic liquids and other electrolytes (under conditions outlined in the Introduction). The free energy of interaction (the potential of mean force) between constituent particles of the liquid are investigated, with emphasis on screened electrostatic interactions. The ions and other particles can have any internal charge distributions and arbitrary shapes.

The decay of the screened electrostatic potential and the free energy of interaction between the particles in ionic liquids can be exponentially damped oscillatory or plain exponential with a large decay length. In the latter case the decay is proportional to $\exp(-\kappa r)/r$ for large r and in the former case there is also a sinusoidal factor. Both behaviors are in agreement with the exact analysis. The plain exponential decay can, for example, occur when there exist high degrees of association between anions and cations – not necessarily from an actual ion pairing, but also from collective associations due to, for example, attractions resulting from strong ion-ion correlations. The analysis in this paper gives insights into these matters in a quite concrete and lucid manner.

In the exact Dressed Ion Theory formalism used in this work, the nonlocal nature of electrostatic interactions in electrolytes, which is due to the ion-ion correlations, is expressed in terms of "dressed ions" – a kind of effective ionic entities ("quasi-particles") – each consisting of a bare ion and a charge density ρ_j^{dress} surrounding the ion. This dress is a well-defined part of the ion cloud around each ion (it consists of the cloud minus the linear part of the polarization response due to the ion). The total charge density ρ_j^* of a dressed ion is the sum of ion's internal charge density and ρ_j^{dress}. In DIT the effects of nonlinear electrostatic response and several complicated ion correlation effects in the electrolyte are included via the dresses of the ions and other particles. Thereby, the DIT formalism makes it possible to express many features of ionic liquids and other electrolytes in a linear response language – a feature that makes DIT physically transparent and yet exact.

Several dielectric features of ionic liquids and other electrolytes are expressed in terms of effective relative permittivities ($\mathcal{E}_r^*$ and $\mathcal{E}_r^{\mathrm{eff}}$), which take some roles that the dielectric constant ε_r has for pure polar liquids consisting of electroneutral molecules. In contrast to ε_r, which can be expressed solely in terms of dipolar features of the molecules, the effective permittivities of ionic liquids have contributions also from quadrupolar, octupolar and higher multipolar features of the constituent particles. The meaning of polarity of an ionic liquid as expressed by the permittivity is not the same as for a pure polar liquid. For ionic liquids with small screening length the difference is larger than for those with a large screening length.

The effective permittivity $\mathcal{E}_r^*$ occurs in the equation for the decay parameter κ that in exact theory replaces the classical expression for the Debye-Hückel screening parameter κ_{DH} in Eq. (1), i.e.,

$$\kappa^2 = \frac{\beta}{\mathcal{E}_r^*(\kappa)\varepsilon_0} \sum_j n_j^{\mathrm{b}} q_j q_j^*, \tag{103}$$

where q_j^* is the charge of the dressed ion (the integral of the dressed ion charge density ρ_j^*) – a "renormalized" charge of an ion of species j. This equation is equivalent to

$$\kappa^2 = -\frac{1}{\varepsilon_0} \int d\mathbf{r} \frac{\sinh(\kappa r)}{\kappa r} \chi^*(r), \tag{104}$$

where $\chi^*(r)$ is the polarization response function for the polarization charge density of a bulk ionic liquid exposed to a perturbing electrostatic field in the linear response domain. The function χ^* expresses this charge density in terms of the total field and is closely related to the static electric susceptibility and the static dielectric function [in Fourier space the susceptibility is $\tilde{\chi}(k) = \tilde{\chi}^*(k)\tilde{\phi}_{\mathrm{Coul}}(k)$ and $\tilde{\epsilon}(k) = 1 - \tilde{\chi}(k)$]. Eqs. (103) and (104) are consequences of the non-local nature of the electrostatics in ionic liquids and other electrolytes. Both $\chi^*(r)$ and $\tilde{\epsilon}(k)$ can be expressed in terms of ρ_j^* for all species present.

The other effective permittivity $\mathcal{E}_r^{\mathrm{eff}}$ gives the far-field magnitude of the screened Coulomb potential $\phi_{\mathrm{Coul}}^*(r)$, that governs the spatial propagation of the electrostatic interactions in an ionic liquid and other electrolytes. When the electrostatic interactions decay in the plain exponential fashion, $\phi_{\mathrm{Coul}}^*(r)$ decays like $A\exp(-\kappa r)/r$ for large r, where $A = 1/[4\pi\mathcal{E}_r^{\mathrm{eff}}\varepsilon_0]$ and the decay length is $\lambda = 1/\kappa$. For the exponentially damped oscillatory case, the decay parameter κ is complex-valued, $\kappa = \kappa_{\Re} \pm i\kappa_{\Im}$, and the potential $\phi_{\mathrm{Coul}}^*(r)$ decays like $B\exp(-\kappa_{\Re}r)\cos(\kappa_{\Im}r + \vartheta_{\mathsf{E}})/r$, i.e., with a decay length $\lambda = 1/\kappa_{\Re}$, a wave length $2\pi/\kappa_{\Im}$ and a phase shift ϑ_{E}. Here $B = 1/(2\pi|\mathcal{E}_r^{\mathrm{eff}}|\varepsilon_0)$ and ϑ_{E} is given by the phase of $\mathcal{E}_r^{\mathrm{eff}}$, which like κ is complex-valued in this case. Here $|\mathcal{E}_r^{\mathrm{eff}}|$ has the role of an effective relative permittivity.

There are in general several terms in $\phi_{\mathrm{Coul}}^*(r)$ with different decay parameters, i.e., solutions κ, κ' etc. to Eqs. (103) and (104). For the plain exponential case we have $\phi_{\mathrm{Coul}}^*(r) \sim A\exp(-\kappa r)/r + A'\exp(-\kappa' r)/r$ with $\kappa < \kappa'$ and each term has its own value of $\mathcal{E}_r^{\mathrm{eff}} = \mathcal{E}_r^{\mathrm{eff}}(\kappa)$, so $A = 1/[4\pi\mathcal{E}_r^{\mathrm{eff}}(\kappa)\varepsilon_0]$ and $A' = 1/[4\pi\mathcal{E}_r^{\mathrm{eff}}(\kappa')\varepsilon_0]$. The other effective permittivity, $\mathcal{E}_r^* = \mathcal{E}_r^*(\kappa)$, has likewise different values for each decay mode. There can also simultaneously be both plain exponential and oscillatory terms with different decay lengths in $\phi_{\mathrm{Coul}}^*(r)$. For smaller r, short-range terms with other decay behavior also contribute.

The average electrostatic potential ψ_i due to an ion of species i and the screened electrostatic pair potential w_{ij}^{el} between any two ions are determined for *all* distances by ϕ_{Coul}^* and the dressed ion charge densities ρ_i^* and ρ_j^* associated with the ions. These two potentials can be obtained by a simple application of Coulomb's law with $\phi_{\mathrm{Coul}}^*(r)$ inserted instead of the usual (unscreened) Coulomb potential $\phi_{\mathrm{Coul}}(r)$ [Eqs. (19), (20), (67) and (71)]. The same applies to ψ_i and w_{ij}^{el} for any particles present in the liquid in addition to the ions. The screened electrostatic pair potential w_{ij}^{el} is a term[43] in the total pair potential of mean force w_{ij} and for the cases considered in this work it dominates in w_{ij} for large distances.

Even if there are some oscillations in the interaction potential for short distances, the decay of the potential can ultimately turn into a plain exponential one further out. What is sufficient for the ultimate decay to take over depends on the system; in many cases the distances need not be very large (sometimes as short as about a couple of ionic diameters). Whether the ultimate decay is plain exponential or exponentially damped oscillatory is determined by the bulk properties of the ionic liquid and is common for the electrostatic interactions between all particles of the system. The relative magnitudes of the plain exponential and the oscillatory parts of the decay of w_{ij}^{el}, when present simultaneously, depend on the properties of the i and j particles and are in general different for the different kinds of particles in the liquid (the same applies for the interaction with or between surfaces). There can also be short-ranged oscillations in w_{ij} that are not governed by $\phi^*_{\mathrm{Coul}}(r)$. The existence of such oscillations in the interaction at small separations between two particles (or surfaces) depends on the properties of each individual particle (or surface) involved. They can exist for some kinds of particles in the liquid but not necessarily for all.

The static dielectric function can be written as a sum of two parts, $\tilde{\epsilon}(k) = \tilde{\epsilon}_{\mathrm{reg}}(k) + \tilde{\epsilon}_{\mathrm{sing}}(k)$. The singular part $\tilde{\epsilon}_{\mathrm{sing}}(k)$, i.e., the part that diverges to infinity like k^{-2} when $k \to 0$ for an electrolyte, can be expressed in terms of the dressed ion charges q_j^* via a factor $\sum_j n_j^{\mathrm{b}} q_j q_j^*$ which gives the magnitude of $\tilde{\epsilon}_{\mathrm{sing}}(k)$ [Eq. (32)]. The remainder, the regular part $\tilde{\epsilon}_{\mathrm{reg}}(k)$, is finite at $k = 0$. The effective relative permittivities $\mathcal{E}_r^{\mathrm{eff}}$ and $\mathcal{E}_r^*$ can be calculated from $\tilde{\epsilon}_{\mathrm{reg}}(k)$ or the polarization response function $\chi^*(r)$ [Eqs. (40), (46) and (48)]. The physical meaning of these formulas is that the permittivities are obtained from the polarization response function by extracting a component at the length scale corresponding to the exponential decay length given by κ, which is appropriate in electrolytes where the potential is exponentially screened. Experimental or theoretical estimates of effective dielectric permittivities of ionic liquids *must correctly include contributions at nonzero wavenumber k in order to be appropriate in general.*

When there is transient ion pairing, $\mathcal{E}_r^*$ and $\mathcal{E}_r^{\mathrm{eff}}$ contains contributions from the ion pairs that are similar to the dipolar contributions to the dielectric constant for polar liquids. In cases with a very large amount of ion pairing, the renormalized charges of the ions become small since pairs contribute little to q_j^* and free ions give a small contribution too since they are in a minority (q_j^* is an average over both free and associated ions). This makes κ from Eq. (103) small, i.e., the screening length is large despite that the number density of ions n_j^{b} is large (n_j^{b} includes all ions of each species). In addition, when $\mathcal{E}_r^*$ is large we can obtain a small κ even if q_j^* for all j are not very small. Note that q_j^* can be small even in absence of ion pairing. It is sufficient that there is a very strong effective anion-cation attraction so each ion has an immediate neighborhood with a charge density of opposite sign that is brought there for instance by many-body correlations among the ions, i.e., in addition to the bare anion-cation Coulomb attraction. The value of $\tilde{\epsilon}_{\mathrm{reg}}(k)$ at $k = 0$, which is the limit of infinite decay length (as well as infinite wave length), is appropriate as an approximation for $\mathcal{E}_r^{\mathrm{eff}}$ and $\mathcal{E}_r^*$ in any case with very long decay length, but not otherwise.

The decay parameter κ and the permittivity $\mathcal{E}_r^*$ can also be expressed in terms of particle specific entities $\mathsf{Q}_i^{\mathrm{eff}}$ for the various species i present in the electrolyte [Eqs. (79) and (82)]. A major role for this entity, which is defined in terms of ρ_i^*, is also to give the magnitude of the average electrostatic potential ψ_i due to a particle with orientation $\boldsymbol{\omega}$. For large r this potential is given by $\psi_i(\mathbf{r}, \boldsymbol{\omega}) \sim \mathsf{Q}_i^{\mathrm{eff}}(\hat{\mathbf{r}}, \boldsymbol{\omega})\phi_{\mathrm{Coul}}^*(r)$ when κ is real (with $\mathbf{r}$ counted from the center of the particle). $\mathsf{Q}_i^{\mathrm{eff}}$ and thereby ψ_i depend on the direction of $\mathbf{r}$, as indicted by $\hat{\mathbf{r}} = \mathbf{r}/r$. Likewise, the magnitude of the potential of mean force between two particles at large distances decays like $\phi_{\mathrm{Coul}}^*(r)$ times the product of the effective entities $\mathsf{Q}_i^{\mathrm{eff}}$ for each particle [Eq. (86)]. When the screened Coulomb potential is exponentially damped oscillatory, each particle contributes also with a direction-dependent phase shift to the oscillations in these potentials, i.e., in addition to the magnitude expressed by $|\mathsf{Q}_i^{\mathrm{eff}}|$ [Eqs. (95) and (96)].

The entity $\mathsf{Q}_i^{\mathrm{eff}}(\hat{\mathbf{r}}, \boldsymbol{\omega})$ can be resolved into an effective charge, $\mathcal{Q}_i^{\mathrm{eff}}$, effective dipole moment, $\boldsymbol{\mu}_i^{\mathrm{eff}}(\boldsymbol{\omega})$, quadrupole moment, $\boldsymbol{\Theta}_i^{\mathrm{eff}}(\boldsymbol{\omega})$, and higher effective multipole moments of the particle. This is the basis of an expansion of $\mathcal{E}_r^*$ in terms of the multipolar features of the constituent ions [Eq. (97)]. Formally, this is done by utilizing multipolar expansions of the static dielectric function $\tilde{\epsilon}(k)$ [Eq. (102)]. Furthermore, the expansion of $\tilde{\epsilon}(k)$ is used to derive simplified expressions for $\mathcal{E}_r^*$ when κ is small [Eqs. (99) and (101)].

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Appendix A: On dressed ion charge density, screened Coulomb potential and $\tilde{\epsilon}(k)$

In this appendix we derive some explicit expressions for the dressed ion charge density ρ_i^* in terms of other entities and consider some issues regarding the calculation of ρ_i^* for an electrolyte with spherical ions. Furthermore we investigate some issues regarding the dielectric function $\tilde{\epsilon}(k)$ and the screened Coulomb potential $\phi_{\mathrm{Coul}}^*(r)$.

1. The charge density of dressed ions

In this section we will show how to obtain the dressed ion charge density $\rho_i^*(r)$ and its charge q_i^* from other more accessible functions like $g_{ij}(r)$, $\psi_i(r)$ and $\rho_i^{\rm tot}(r)$. Starting from the Fourier transform of Eq. (19) and Eq. (35) we can derive

$$\begin{aligned}\tilde{\rho}_i^*(k) &= \frac{\tilde{\psi}_i(k)}{\tilde{\phi}^*_{\rm Coul}(k)} = \varepsilon_0 k^2 \tilde{\epsilon}(k)\tilde{\psi}_i(k)\\ &= \frac{\varepsilon_0 k^2 \tilde{\psi}_i(k)}{1-\beta\sum_j q_j n_j^{\rm b}\tilde{\psi}_j(k)} = \frac{\tilde{\rho}_i^{\rm tot}(k)}{1-\beta\sum_j q_j n_j^{\rm b}\tilde{\rho}_j^{\rm tot}(k)/(\varepsilon_0 k^2)},\end{aligned} \tag{A1}$$

where we have used Eq. (A6) (derived in the next Appendix section) and the Fourier transform of Eq. (8) to obtain the last two equalities. If we know $\tilde{\psi}_i(k)$ or $\tilde{\rho}_i^{\rm tot}(k)$ we can accordingly calculate $\tilde{\rho}_i^*(k)$. For $k=0$, however, Eq. (A1) cannot be used as it stands because the rhs becomes indeterminate when $k\to 0$ since both the numerator and denominator go to zero like k^2. Note that that $\beta\sum_i q_i n_i^{\rm b}\tilde{\psi}_i(k)\to 1$ when $k\to 0$, which is equivalent[68] to the Stillinger-Lovett second moment condition.[69] The latter can be written as

$$\beta\sum_i q_i n_i^{\rm b}\int d\mathbf{r}\, r^2\rho_i^{\rm tot}(r) = -6\varepsilon_0, \tag{A2}$$

in our notation.

To obtain $\tilde{\rho}_i^*(k)$ for small k, we make an expansion of the Fourier transform of $\rho_i^{\rm tot}$

$$\begin{aligned}\tilde{\rho}_i^{\rm tot}(k) &= \int d\mathbf{r}\frac{\sin(kr)}{kr}\rho_i^{\rm tot}(r)\\ &= -\frac{k^2}{3!}\int d\mathbf{r}\, r^2\rho_i^{\rm tot}(r) + \frac{k^4}{5!}\int d\mathbf{r}\, r^4\rho_i^{\rm tot}(r) + \mathcal{O}(k^6)\end{aligned} \tag{A3}$$

where we have expanded $\sin(kr)$ in a power series and used the fact that $\int d\mathbf{r}\rho_i^{\rm tot}(r)=0$ due to local electroneutrality. By inserting Eq. (A3) into Eq. (A1) and using Eq. (A2) we obtain

$$q_i^* = \tilde{\rho}_i^*(0) = \frac{20\varepsilon_0\int d\mathbf{r}\, r^2\rho_i^{\rm tot}(r)}{\beta\sum_j q_j n_j^{\rm b}\int d\mathbf{r}\, r^4\rho_j^{\rm tot}(r)}. \tag{A4}$$

The small k dependence of $\tilde{\rho}_i^*(k)$ can be extracted from Eq. (A1) in terms of higher moments of $\rho_i^{\rm tot}(r)$ from the expansion obtained by utilizing further terms in the k expansion of $\tilde{\rho}_i^{\rm tot}(k)$ in an analogous manner. This is useful since a direct application of Eq. (A1) for small k is numerically difficult. From $\tilde{\rho}_i^*(k)$ one can calculate $\rho_i^*(r)$ and all relevant quantities like $\chi^*(r)$, κ, $\mathcal{E}_r^{\rm eff}$, $\mathcal{E}_r^*$ etc.

More fundamentally, $\rho_i^*(r) = q_i\delta^{(3)}(r) + \rho_i^{\mathrm{dress}}(r)$ can be defined[35] in terms of pair distribution functions in a similar manner as the definition of $\rho_i(r)$ in Eq. (4), namely

$$\rho_i^{\mathrm{dress}}(r) = \sum_j q_j n_j^{\mathrm{b}} g_{ij}^*(r),$$

where $g_{ij}^*(r)$ is defined from the direct correlation function $c_{ij}(r)$ of the fluid in the following manner. The total correlation function $h_{ij}(r) = g_{ij}(r) - 1$ and $c_{ij}(r)$ satisfy the Ornstein-Zernike (OZ) equation,[70] which can be solved to obtain $c_{ij}(r)$ from $h_{ij}(r)$. The short range part of $c_{ij}(r)$ is given by $c_{ij}^*(r) \equiv c_{ij}(r) + \beta q_i q_j \phi_{\mathrm{Coul}}(r)$. The functions $h_{ij}^*(r) \equiv g_{ij}^*(r) - 1$ and $c_{ij}^*(r)$ also satisfy the OZ equation,[35] so $h_{ij}^*(r)$ and hence $g_{ij}^*(r)$ can be obtained from $c_{ij}^*(r)$ by solving the OZ equation once more. A numerical procedure to do this conversion from $g_{ij}(r)$ determined by computer simulations is described in Ref. [55] (see also Ref. [71]).

2. The reciprocal dielectric function

The dielectric function in Eq. (28) can for the case of spherical ions be written

$$\tilde{\epsilon}(k) = 1 + \frac{\beta}{\varepsilon_0 k^2}\sum_i q_i n_i^{\mathrm{b}} \tilde{\rho}_i^*(k), \tag{A5}$$

where we have used Eq. (13) and $\tilde{\phi}_{\mathrm{Coul}}(k) = 1/(\varepsilon_0 k^2)$. By first inserting $1/(\varepsilon_0 k^2) = \tilde{\phi}_{\mathrm{Coul}}(k) = \tilde{\phi}_{\mathrm{Coul}}^*(k)\tilde{\epsilon}(k)$ and then the Fourier transform of Eq. (19) into this equation we obtain

$$\tilde{\epsilon}(k) = 1 + \beta\sum_i q_i n_i^{\mathrm{b}} \tilde{\rho}_i^*(k)\tilde{\phi}_{\mathrm{Coul}}^*(k)\tilde{\epsilon}(k) = 1 + \beta\sum_i q_i n_i^{\mathrm{b}} \tilde{\psi}_i(k)\tilde{\epsilon}(k).$$

This yields

$$\frac{1}{\tilde{\epsilon}(k)} = 1 - \beta\sum_i q_i n_i^{\mathrm{b}} \tilde{\psi}_i(k) = 1 - \frac{\beta}{\varepsilon_0 k^2}\sum_i q_i n_i^{\mathrm{b}} \tilde{\rho}_i^{\mathrm{tot}}(k), \tag{A6}$$

where the last equality is obtained by using $\tilde{\psi}_i(k) = \tilde{\rho}_i^{\mathrm{tot}}(k)\tilde{\phi}_{\mathrm{Coul}}(k)$. We can write this as the familiar expression for $\tilde{\epsilon}(k)$

$$\frac{1}{\tilde{\epsilon}(k)} = 1 - \frac{\beta}{\varepsilon_0 k^2}\tilde{S}_{QQ}(k), \tag{A7}$$

where $\tilde{S}_{QQ}(k) = \sum_{ij} q_i q_j [n_i^{\mathrm{b}}\delta_{ij} + \sum_i n_i^{\mathrm{b}} n_j^{\mathrm{b}} \tilde{h}_{ij}(k)]$ is the the charge-charge structure factor and $h_{ij} = g_{ij} - 1$.

The reciprocal dielectric function can be expanded in a power series $1/\tilde{\epsilon}(k) = b_0 + b_2 k^2 + b_4 k^4 + \mathcal{O}(k^6)$. The coefficients can be expressed in terms of $\rho_i^{\mathrm{tot}}(r)$ as follows. From the second moment condition (A2) follows that b_0 is zero, as it must since $\tilde{\epsilon}(k)$ diverges at $k=0$, and from the k^4 term in Eq. (A3) we can deduce that

$$b_2 = -\frac{\beta}{120\varepsilon_0}\sum_i q_i n_i^{\mathrm{b}} \int d\mathbf{r}\, r^4 \rho_i^{\mathrm{tot}}(r). \tag{A8}$$

Likewise b_4 can be expressed in terms of the sixth moment of $\rho_i^{\mathrm{tot}}(r)$ by taking the expansion one step further. (For nonspherical particles, see Appendix B 4.)

Since $\tilde{\epsilon}(k) = [b_2k^2 + b_4k^4 + \mathcal{O}(k^6)]^{-1} = 1/(b_2k^2) - b_4/(b_2)^2 + \mathcal{O}(k^2)$, the singular part of the dielectric function can be written $\tilde{\epsilon}_{\mathrm{sing}}(k) = 1/(b_2k^2)$ and we have $\tilde{\epsilon}_{\mathrm{reg}}(0) = -b_4/(b_2)^2$. The Taylor series of $\tilde{\epsilon}_{\mathrm{reg}}(k)$ can be obtained by evaluating further terms in the same manner. Note that it follows from Eq. (A4) that the coefficient of $\tilde{\epsilon}_{\mathrm{sing}}(k)$ in Eq. (32) can be expressed as

$$\frac{\beta}{\varepsilon_0}\sum_i n_i^{\mathrm{b}} q_i q_i^* = -\frac{120\varepsilon_0}{\beta\sum_j q_j n_j^{\mathrm{b}}\int d\mathbf{r}\, r^4\rho_j^{\mathrm{tot}}(r)} = \frac{1}{b_2}, \tag{A9}$$

where we have applied Eq. (A2). The k^4 coefficient in $\tilde{S}_{QQ}(k)$ and hence the $1/k^2$ coefficient in $\tilde{\epsilon}(k)$ can also be determined in terms of a derivative of the mean chemical potential with respect to charge density by using hydrodynamic arguments.[72]

3. The screened Coulomb potential and the dielectric function

The decay behavior of $\phi^*_{\mathrm{Coul}}(r)$ shown in Eq. (45) was derived in Ref. [35] from $\tilde{\phi}^*_{\mathrm{Coul}}(k) = [\varepsilon_0 k^2\tilde{\epsilon}(k)]^{-1}$ by residue calculus in complex Fourier space (in Ref. [35] $\phi^*_{\mathrm{Coul}}(r)\delta q$, where δq is an infinitesimally small point charge, is denoted $\delta\Psi^{\mathrm{av}}(r)$). This decay can alternatively (and equivalently) be obtained in the following, more elementary manner. Since the denominator of $\tilde{\phi}^*_{\mathrm{Coul}}(k)$ has a zero at $k = \mathrm{i}\kappa$ (and therefore also a zero at $k=-\mathrm{i}\kappa$), it satisfies $\varepsilon_0 k^2\tilde{\epsilon}(k) \sim \varepsilon_0 C(k^2+\kappa^2)$ in the limit $k\to \mathrm{i}\kappa$, where C is a constant. This constant is equal to the limit of $k^2\tilde{\epsilon}(k)/(k^2+\kappa^2)$ when $k\to\mathrm{i}\kappa$. We have

$$\begin{aligned}\frac{k^2\tilde{\epsilon}(k)}{k^2+\kappa^2} &\to \left[\frac{2k\tilde{\epsilon}(k) + k^2 d\tilde{\epsilon}(k)/dk}{2k}\right]_{k=\mathrm{i}\kappa}\\ &= \left[\frac{k d\tilde{\epsilon}(k)/dk}{2}\right]_{k=\mathrm{i}\kappa},\end{aligned}$$

where we have used l'Hospital's rule and the fact that $\tilde{\epsilon}(\mathrm{i}\kappa)=0$. Thus $C = \mathcal{E}_r^{\mathrm{eff}}$ where

$$\mathcal{E}_r^{\mathrm{eff}} = \left[\frac{k}{2}\frac{d\tilde{\epsilon}(k)}{dk}\right]_{k=\mathrm{i}\kappa}, \tag{A10}$$

$$\tilde{\phi}^*_{\mathrm{Coul}}(k) \sim \frac{1}{\mathcal{E}_r^{\mathrm{eff}}\varepsilon_0(k^2+\kappa^2)} \tag{A11}$$

in the limit $k \to \mathrm{i}\kappa$. The rhs of Eq. (A11) is the Fourier transform of the rhs of Eq. (45), which hence follows. Note that since $\tilde{\psi}_i(k) = \tilde{\rho}_i^*(k)\tilde{\phi}^*_{\mathrm{Coul}}(k)$ for spherical ions (from Eq. (19)), we have in the same limit $\tilde{\psi}_i(k) \sim q_i^{\mathrm{eff}}/[\mathcal{E}_r^{\mathrm{eff}}\varepsilon_0(k^2+\kappa^2)]$, where $q_i^{\mathrm{eff}} = \tilde{\rho}_i^*(i\kappa)$ [the latter can alternatively be written as in Note [46], cf. Eq. (88)]. This implies that $\psi_i(r) \sim q_i^{\mathrm{eff}}\phi^*_{\mathrm{Coul}}(r)$ when $r \to \infty$ for spherical ions (cf. Ref. [35]). Likewise, since $\tilde{w}_{ij}^{\mathrm{el}}(k) = \tilde{\rho}_i^*(k)\tilde{\rho}_j^*(k)\tilde{\phi}^*_{\mathrm{Coul}}(k)$ (from Eq. (20)) we have $w_{ij}(r) \sim q_i^{\mathrm{eff}}q_j^{\mathrm{eff}}\phi^*_{\mathrm{Coul}}(r)$.

To write $\mathcal{E}_r^{\mathrm{eff}}$ in terms of $\chi^*(r)$, it is useful to write Eq. (A10) as $\mathcal{E}_r^{\mathrm{eff}} = \frac{1}{2}\left[d(k\tilde{\epsilon}(k))/dk\right]_{k=\mathrm{i}\kappa}$, where we have used the fact that $\tilde{\epsilon}(\mathrm{i}\kappa) = 0$. By inserting the definition (28) of $\tilde{\epsilon}(k)$, one can write this as

$$\mathcal{E}_r^{\mathrm{eff}} = \frac{1}{2}\left[3 - \frac{1}{\varepsilon_0 k^2}\frac{d[k\tilde{\chi}^*(k)]}{dk}\right]_{k=\mathrm{i}\kappa}. \tag{A12}$$

Using Eq. (26), one can write Eq. (A12) as in Eq. (46).

One can express $\mathcal{E}_r^{\mathrm{eff}}$ in term of $\tilde{\epsilon}_{\mathrm{reg}}(k)$. By inserting Eq. (29) into Eq. (A10) we have

$$\mathcal{E}_r^{\mathrm{eff}} = \left[\frac{k}{2}\frac{d\tilde{\epsilon}_{\mathrm{sing}}(k)}{dk} + \frac{k}{2}\frac{d\tilde{\epsilon}_{\mathrm{reg}}(k)}{dk}\right]_{k=\mathrm{i}\kappa} = \left[-\tilde{\epsilon}_{\mathrm{sing}}(k) + \frac{k}{2}\frac{d\tilde{\epsilon}_{\mathrm{reg}}(k)}{dk}\right]_{k=\mathrm{i}\kappa},$$

where we have used $k[d(k^{-2})/dk] = -2/k^2$. It follows that

$$\mathcal{E}_r^{\mathrm{eff}} = \left[\tilde{\epsilon}_{\mathrm{reg}}(k) + \frac{k}{2}\frac{d\tilde{\epsilon}_{\mathrm{reg}}(k)}{dk}\right]_{k=\mathrm{i}\kappa}, \tag{A13}$$

where we have used the fact that $\tilde{\epsilon}_{\mathrm{reg}}(\mathrm{i}\kappa) + \tilde{\epsilon}_{\mathrm{sing}}(\mathrm{i}\kappa) = 0$. This result can also be derived from Eqs. (31), (39), and (46).

Appendix B: Expansions of $\tilde{\epsilon}(k)$ for liquids with arbitrarily shaped particles

In this appendix we shall consider the dielectric function in Eq. (69), which we can write

$$\tilde{\epsilon}(k) = 1 + \frac{\beta}{\varepsilon_0 k^2}\sum_j n_j^{\mathrm{b}}\left\langle \underline{\tilde{\rho}_j^*}(\mathbf{k},\boldsymbol{\omega})\tilde{\sigma}_j(\mathbf{k},\boldsymbol{\omega})\right\rangle_{\boldsymbol{\omega}}, \tag{B1}$$

where

$$\tilde{\sigma}_j(\mathbf{k},\boldsymbol{\omega}) = \int d\mathbf{r}\sigma_j(\mathbf{r},\boldsymbol{\omega})e^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \tag{B2}$$

and analogously for $\tilde{\rho}_j^*$. Underline indicates complex conjugation. We will obtain a multipolar expansion of $\tilde{\epsilon}(k)$ by making an expansion of $\exp(-\mathrm{i}\mathbf{k}\cdot\mathbf{r})$ in the expressions for $\tilde{\sigma}_j$ and $\tilde{\rho}_j^*$ and insert this into Eq. (B1). Thereby it is advantageous to consistently utilize traceless multipole moments of the kind used in Section III rather than multipole moments with nonzero trace like a quadrupolar $\int d\mathbf{r}\sigma_j(\mathbf{r},\boldsymbol{\omega})\mathbf{rr}$ and an octupolar $\int d\mathbf{r}\sigma_j(\mathbf{r},\boldsymbol{\omega})\mathbf{rrr}$ moment. The latter would appear if we do a simple Taylor expansion of the exponential function in Eq. (B2), i.e., $\sum_\nu(-\mathrm{i}\mathbf{k}\cdot\mathbf{r})^\nu/\nu!$. Instead we will use the Rayleigh expansion[56] of the exponential function. (At the end of section B 3 below we will make a brief remark on the difference between the two alternative multipole moments.) From the multipolar expansion of $\tilde{\epsilon}(k)$ we will then obtain its power series expansion in k.

The method we use will also be utilized to expand $1/\tilde{\epsilon}(k)$ given by the relationship

$$\frac{1}{\tilde{\epsilon}(k)} = 1 - \frac{\beta}{\varepsilon_0 k^2}\sum_j n_j^{\mathrm{b}} \left\langle \underline{\tilde{\rho}_j^{\mathrm{tot}}}(\mathbf{k},\boldsymbol{\omega})\tilde{\sigma}_j(\mathbf{k},\boldsymbol{\omega})\right\rangle_{\boldsymbol{\omega}}, \tag{B3}$$

which corresponds to Eqs. (A6) and (A7), but we will focus of Eq. (B1) to start with.

1. Spherical tensor expansion

The Rayleigh expansion of the exponential function is[56]

$$e^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} = 4\pi\sum_{l,m}\mathrm{i}^l\, j_l(kr)\underline{Y_{lm}}(\hat{\mathbf{r}})Y_{lm}(\hat{\mathbf{k}}), \tag{B4}$$

where $j_l(x)$ is a spherical Bessel function of order l, $Y_{lm}(\hat{\mathbf{r}})$ is a spherical harmonics with $\hat{\mathbf{r}}$ representing the the azimuthal and polar angles (φ_r,θ_r) and the sums are taken over $l = 0,1,\ldots,\infty$ and $-l \leq m \leq l$. By inserting this expansion in Eq. (B2) we obtain

$$\tilde{\sigma}_j(\mathbf{k},\boldsymbol{\omega}) = 4\pi\sum_{l,m}\int d\mathbf{r}\sigma_j(\mathbf{r},\boldsymbol{\omega})(-\mathrm{i})^l\, j_l(kr)\underline{Y_{lm}}(\hat{\mathbf{r}})Y_{lm}(\hat{\mathbf{k}})$$

and by defining

$$\tilde{\sigma}_{j;lm}(k,\boldsymbol{\omega}) = (2l+1)!!\int d\mathbf{r}\, r^l\sigma_j(\mathbf{r},\boldsymbol{\omega})\frac{j_l(kr)}{(kr)^l}\underline{Y_{lm}}(\hat{\mathbf{r}}) \tag{B5}$$

we can write this as

$$\tilde{\sigma}_j(\mathbf{k},\boldsymbol{\omega}) = 4\pi\sum_{l,m}\frac{(-\mathrm{i}k)^l}{(2l+1)!!}\tilde{\sigma}_{j;lm}(k,\boldsymbol{\omega})Y_{lm}(\hat{\mathbf{k}}). \tag{B6}$$

Note that $j_l(x)/x^l \to 1/(2l+1)!!$ when $x \to 0$, which motivates the factor in front of the integral in the definition of $\tilde{\sigma}_{j;lm}$. For $k = 0$ the quantity $\sigma_{j;lm}$ constitutes the mth component of the spherical multipole moment tensor of order l of the charge distribution σ_j defined as[57]

$$\begin{aligned} M_{j;lm}(\boldsymbol{\omega}) &= \int d\mathbf{r}\, r^l \sigma_j(\mathbf{r},\boldsymbol{\omega})\underline{Y_{lm}}(\hat{\mathbf{r}}) \\ &= \int d\mathbf{r}\, \sigma_j(\mathbf{r},\boldsymbol{\omega})\underline{\mathcal{Y}_{lm}}(\mathbf{r}) \end{aligned}$$

where $\mathcal{Y}_{lm}(\mathbf{r}) = r^l Y_{lm}(\hat{\mathbf{r}})$ is a solid harmonics, i.e., a homogeneous harmonic polynomial in x, y and z.

Likewise, for $\tilde{\rho}^*_j(\mathbf{k},\boldsymbol{\omega})$ we have a relationship corresponding to Eq. (B6) with $\tilde{\rho}^*_{j;lm}(k,\boldsymbol{\omega})$ defined analogously to Eq. (B5). We can write the definition of $\tilde{\rho}^*_{j;lm}$ as

$$\tilde{\rho}^*_{j;lm}(k,\boldsymbol{\omega}) = (2l+1)!! \int d\mathbf{r}\, \rho^*_j(\mathbf{r},\boldsymbol{\omega}) \frac{j_l(kr)}{(kr)^l}\underline{\mathcal{Y}_{lm}}(\mathbf{r}), \tag{B7}$$

where we have entered $\underline{\mathcal{Y}_{lm}}$ instead of $r^l \underline{Y_{lm}}$. Furthermore, we define spherical multipole moment tensor for ρ^*_j as

$$M^*_{j;lm}(\boldsymbol{\omega}) = \int d\mathbf{r}\, \rho^*_j(\mathbf{r},\boldsymbol{\omega})\underline{\mathcal{Y}_{lm}}(\mathbf{r}).$$

By utilizing these results we can write

$$\begin{aligned} \underline{\tilde{\rho}^*_j}(\mathbf{k},\boldsymbol{\omega})\tilde{\sigma}_j(\mathbf{k},\boldsymbol{\omega}) = (4\pi)^2 \sum_{l',m'}\sum_{l,m} &\frac{(\mathrm{i}k)^{l'}(-\mathrm{i}k)^l}{(2l'+1)!!(2l+1)!!} \\ &\times \underline{\tilde{\rho}^*_{j;l'm'}}(k,\boldsymbol{\omega})\tilde{\sigma}_{j;lm}(k,\boldsymbol{\omega})\underline{Y_{l'm'}}(\hat{\mathbf{k}})Y_{lm}(\hat{\mathbf{k}}), \end{aligned}$$

which we can insert in Eq. (B1). Since the rhs of the latter equation does not depend on the direction $\hat{\mathbf{k}}$ due to the averaging over orientations, we can take the average of $\underline{\tilde{\rho}^*_j}\tilde{\sigma}_j$ over all directions of $\hat{\mathbf{k}}$, whereby we can utilize the orthonormality of the spherical harmonics

$$\int d\hat{\mathbf{k}}\, \underline{Y_{l'm'}}(\hat{\mathbf{k}})Y_{lm}(\hat{\mathbf{k}}) = \delta_{ll'}\delta_{mm'}$$

and obtain

$$\frac{1}{4\pi}\int d\hat{\mathbf{k}}\, \underline{\tilde{\rho}^*_j}(\mathbf{k},\boldsymbol{\omega})\tilde{\sigma}_j(\mathbf{k},\boldsymbol{\omega}) = 4\pi \sum_l \frac{k^{2l}}{[(2l+1)!!]^2}\sum_m \underline{\tilde{\rho}^*_{j;lm}}(k,\boldsymbol{\omega})\tilde{\sigma}_{j;lm}(k,\boldsymbol{\omega}).$$

The sum over m in the rhs is the inner product of two spherical tensors of order l with components defined in Eqs. (B5) and (B7), i.e., the product

$$\tilde{\rho}^*_{j;l} \star \tilde{\sigma}_{j;l}(k) \equiv \sum_m \underline{\tilde{\rho}^*_{j;lm}}(k,\boldsymbol{\omega})\tilde{\sigma}_{j;lm}(k,\boldsymbol{\omega}). \tag{B8}$$

It is invariant under rotations and hence independent of $\boldsymbol{\omega}$. Hence we finally obtain

$$\tilde{\epsilon}(k) = 1 + \frac{4\pi\beta}{\varepsilon_0}\sum_j n^{\mathrm{b}}_j \sum_l \frac{k^{2(l-1)}}{[(2l+1)!!]^2}\tilde{\rho}^*_{j;l} \star \tilde{\sigma}_{j;l}(k), \tag{B9}$$

where the $l = 0$ term is a product of two scalars, the $l = 1$ term is the product of two vectors written in spherical components etc.

2. Cartesian tensor expansion

It is worthwhile to go over to cartesian tensors starting from the expression (B9). Thereby we will use the relationship[56]

$$\sum_m \mathcal{Y}_{lm}(\mathbf{r})\underline{\mathcal{Y}_{lm}}(\mathbf{r}') = \frac{2l+1}{4\pi}\mathcal{P}_l(\mathbf{r},\mathbf{r}') \tag{B10}$$

where $\mathcal{P}_l(\mathbf{r},\mathbf{r}') = (rr')^l P_l(\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}')$ is a solid Legendre polynomial and $P_l(x)$ is the ordinary Legendre polynomial of order l. By inserting the definitions (B5) and (B7) in Eq. (B8) and use Eq. (B10) we obtain

$$\begin{aligned} \tilde{\rho}^*_{j;l} \star \tilde{\sigma}_{j;l}(k) &= \frac{(2l+1)[(2l+1)!!]^2}{4\pi} \\ \times \int d\mathbf{r}d\mathbf{r}'\, \rho^*_j(\mathbf{r},\boldsymbol{\omega})&\frac{j_l(kr)}{(kr)^l}\sigma_j(\mathbf{r}',\boldsymbol{\omega})\frac{j_l(kr')}{(kr')^l}\mathcal{P}_l(\mathbf{r},\mathbf{r}'). \end{aligned} \tag{B11}$$

To write this in terms of the cartesian components of the tensors we will utilize the relationship[59]

$$\mathcal{P}_l(\mathbf{r},\mathbf{r}') = \frac{l!}{(2l-1)!!}\mathbf{P}_l(\mathbf{r}) \bullet \mathbf{P}_l(\mathbf{r}') \tag{B12}$$

where $\mathbf{P}_l(\mathbf{r})$ is the Legendre polynomial tensor defined below and where $\bullet$ stands for full contraction product (e.g.. if $\mathbf{a} = \{a_{ijk}\}$ and $\mathbf{b} = \{b_{ijk}\}$ then $\mathbf{a}\bullet\mathbf{b} = \sum_{ijk} a_{ijk}b_{ijk}$). Note that by convention $(-1)!! = 1$.

The Legendre polynomial tensor $\mathbf{P}_l(\mathbf{r})$ is a symmetric traceless tensor of order l that is directly related[58–60] to the solid Legendre polynomial via $\mathcal{P}_l(\mathbf{r},\mathbf{r}') = \mathbf{r}^{[l]} \bullet \mathbf{P}_l(\mathbf{r}') = \mathbf{P}_l(\mathbf{r}) \bullet (\mathbf{r}')^{[l]}$, where $\mathbf{r}^{[l]} = \mathbf{rrr}\ldots\mathbf{r}$ [l factors of $\mathbf{r}$] and likewise for $\mathbf{r}'$ (see also Ref. [38]). Explicitly, it is given by

$$\mathbf{P}_l(\mathbf{r}) = \frac{(-1)^l}{l!}r^{2l+1}\boldsymbol{\nabla}^{[l]}\left(\frac{1}{r}\right) = \frac{(-1)^l}{l!}r^{2l+1}\boldsymbol{\nabla\nabla\nabla}\ldots\boldsymbol{\nabla}\left(\frac{1}{r}\right)$$

[with l factors $\boldsymbol{\nabla}$, where $\boldsymbol{\nabla} = (\partial/\partial x, \partial/\partial y, \partial/\partial z)$]. The lowest order Legendre polynomial tensors are shown in Table I together with the corresponding solid Legendre polynomials.

By using Eq. (B12), we can write the integral in the rhs of Eq. (B11) as

$$\begin{aligned} &\int d\mathbf{r}d\mathbf{r}'\, \rho^*_j(\mathbf{r},\boldsymbol{\omega})\frac{j_l(kr)}{(kr)^l}\sigma_j(\mathbf{r}',\boldsymbol{\omega})\frac{j_l(kr')}{(kr')^l}\mathcal{P}_l(\mathbf{r},\mathbf{r}') \\ &= \frac{l!}{(2l-1)!![(2l+1)!!]^2}\tilde{\boldsymbol{\rho}}^{*(l)}_j(k,\boldsymbol{\omega}) \bullet \tilde{\boldsymbol{\sigma}}^{(l)}_j(k,\boldsymbol{\omega}) \end{aligned}$$

where

$$\tilde{\boldsymbol{\rho}}^{*(l)}_j(k,\boldsymbol{\omega}) = (2l+1)!!\int d\mathbf{r}\, \mathbf{P}_l(\mathbf{r})\rho^*_j(\mathbf{r},\boldsymbol{\omega})\frac{j_l(kr)}{(kr)^l} \tag{B13}$$

Table I. The lowest order solid Legendre polynomials $\mathcal{P}_l(\mathbf{r},\mathbf{s})$ and Legendre polynomial tensors $\mathbf{P}_l(\mathbf{r})$. The ordinary Legendre polynomials are denoted $P_l(x)$ and $\mathscr{S}$ stands for a symmetrisation operator for the indices.[a]

$\mathcal{P}_l(\mathbf{r},\mathbf{s}) = (rs)^l P_l(\hat{\mathbf{r}}\cdot\hat{\mathbf{s}})$	$\mathbf{P}_l(\mathbf{r})$
$\mathcal{P}_0 = 1$	$\mathbf{P}_0 = 1$
$\mathcal{P}_1 = \mathbf{r}\cdot\mathbf{s}$	$\mathbf{P}_1 = \mathbf{r}$
$\mathcal{P}_2 = \frac{1}{2}\left[3(\mathbf{r}\cdot\mathbf{s})^2 - r^2s^2\right]$	$\mathbf{P}_2 = \frac{1}{2}\left[3\mathbf{rr} - r^2\mathbb{I}\right]$
$\mathcal{P}_3 = \frac{1}{2}\left[5(\mathbf{r}\cdot\mathbf{s})^3 - 3r^2s^2(\mathbf{r}\cdot\mathbf{s})\right]$	$\mathbf{P}_3 = \frac{1}{2}\left[5\mathbf{rrr} - 3r^2\mathscr{S}\{\mathbf{r}\mathbb{I}\}\right]$
$\mathcal{P}_4 = \frac{1}{8}\left[35(\mathbf{r}\cdot\mathbf{s})^4 - 30r^2s^2(\mathbf{r}\cdot\mathbf{s})^2 + 3r^4s^4\right]$	$\mathbf{P}_4 = \frac{1}{8}\left[35\mathbf{rrrr} - 30r^2\mathscr{S}\{\mathbf{rr}\mathbb{I}\} + 3r^4\mathscr{S}\{\mathbb{I}\mathbb{I}\}\right]$

[a] We have, for example, $\mathscr{S}\{\mathbf{r}\mathbb{I}\}_{\nu\nu'\nu''} = \frac{1}{3}(r_\nu\mathbb{I}_{\nu'\nu''} + r_{\nu'}\mathbb{I}_{\nu\nu''} + r_{\nu''}\mathbb{I}_{\nu\nu'})$.

and

$$\tilde{\boldsymbol{\sigma}}_j^{(l)}(k,\boldsymbol{\omega}) = (2l+1)!!\int d\mathbf{r}'\,\mathbf{P}_l(\mathbf{r}')\sigma_j(\mathbf{r}',\boldsymbol{\omega})\frac{j_l(kr')}{(kr')^l}. \tag{B14}$$

Note that for $k=0$ we have $\tilde{\boldsymbol{\sigma}}_j^{(l)}(0,\boldsymbol{\omega}) = \boldsymbol{\mathcal{M}}_j^{(l)}(\boldsymbol{\omega})$, the multipole moment tensor of the ion of species j defined in Eq. (55). Likewise, at $k=0$ the quantity $\tilde{\boldsymbol{\rho}}_j^{*(l)}$ equals the multipole moment tensor

$$\boldsymbol{\mathcal{M}}_j^{*(l)}(\boldsymbol{\omega}) = \int d\mathbf{r}\,\mathbf{P}_l(\mathbf{r})\rho_j^*(\mathbf{r},\boldsymbol{\omega})$$

of the charge distribution ρ_j^*. We also note that if one inserts $k = \mathrm{i}\kappa$, the values of quantities $\tilde{\rho}_j^{*(l)}$ and $\tilde{\boldsymbol{\sigma}}_j^{(l)}$ become equal to $\boldsymbol{\mathcal{Q}}_j^{\mathrm{eff}(l)}$ and $\boldsymbol{\mathcal{Q}}_j^{(l)}$, respectively, defined in Eqs. (92) and (90).

From Eq. (B11) and the results above we obtain the spherical tensor entity $\tilde{\rho}_{j;l}^* \star \tilde{\sigma}_{j;l}(k)$ expressed in the corresponding Cartesian tensor entity

$$\tilde{\rho}_{j;l}^* \star \tilde{\sigma}_{j;l}(k) = \frac{(2l+1)\,l!}{4\pi(2l-1)!!}\tilde{\boldsymbol{\rho}}_j^{*(l)} \bullet \tilde{\boldsymbol{\sigma}}_j^{(l)}(k),$$

where

$$\tilde{\boldsymbol{\rho}}_j^{*(l)} \bullet \tilde{\boldsymbol{\sigma}}_j^{(l)}(k) \equiv \tilde{\boldsymbol{\rho}}_j^{*(l)}(k,\boldsymbol{\omega}) \bullet \tilde{\boldsymbol{\sigma}}_j^{(l)}(k,\boldsymbol{\omega})$$

is independent of $\boldsymbol{\omega}$. Using Eq. (B9), we can write the dielectric function as

$$\tilde{\varepsilon}(k) = 1 + \frac{\beta}{\varepsilon_0}\sum_j n_j^{\mathrm{b}}\sum_l \frac{k^{2(l-1)}(2l+1)^2\,l!}{[(2l+1)!!]^3}\tilde{\boldsymbol{\rho}}_j^{*(l)} \bullet \tilde{\boldsymbol{\sigma}}_j^{(l)}(k). \tag{B15}$$

Explicitly, we have

$$\tilde{\epsilon}(k) = 1 + \frac{\beta}{\varepsilon_0}\sum_j n_j^{\mathrm{b}}\left[\frac{1}{k^2}\tilde{\rho}_j^{*(0)}(k)\tilde{\sigma}_j^{(0)}(k) + \frac{1}{3}\tilde{\boldsymbol{\rho}}_j^{*(1)}\cdot\tilde{\boldsymbol{\sigma}}_j^{(1)}(k) + \frac{2k^2}{135}\tilde{\boldsymbol{\rho}}_j^{*(2)}\bullet\tilde{\boldsymbol{\sigma}}_j^{(2)}(k) + \dots\right], \tag{B16}$$

where the first term in the square bracket is the product of two scalars, the second is the dot product of two vectors (like dipoles) and the third is the full contraction product of two second order tensors (like quadrupoles).

Consider the regular part of the dielectric function, $\tilde{\epsilon}_{\mathrm{reg}}(k) = \tilde{\epsilon}(k) - \tilde{\epsilon}_{\mathrm{sing}}(k)$, where $\tilde{\epsilon}_{\mathrm{sing}}(k)$ is defined in Eq. (32). The expansion for $\tilde{\epsilon}_{\mathrm{reg}}(k)$ that corresponds to Eq. (B16) is

$$\tilde{\epsilon}_{\mathrm{reg}}(k) = 1 + \frac{\beta}{\varepsilon_0}\sum_j n_j^{\mathrm{b}}\left[\frac{\tilde{\rho}_j^{*(0)}(k)\tilde{\sigma}_j^{(0)}(k) - q_j^* q_j}{k^2} + \frac{1}{3}\tilde{\boldsymbol{\rho}}_j^{*(1)}\cdot\tilde{\boldsymbol{\sigma}}_j^{(1)}(k) + \frac{2k^2}{135}\tilde{\boldsymbol{\rho}}_j^{*(2)}\bullet\tilde{\boldsymbol{\sigma}}_j^{(2)}(k) + \dots\right], \tag{B17}$$

where $q_j^* q_j = \tilde{\rho}_j^{*(0)}(0)\tilde{\sigma}_j^{(0)}(0)$ so the first term in the sum is finite at $k = 0$. The terms beyond the second order term in this expansion follow from Eq. (B15).

$\mathcal{E}_r^*$ is obtained by inserting $k = \mathrm{i}\kappa$ in $\tilde{\epsilon}_{\mathrm{reg}}(k)$. By using the definitions of $\boldsymbol{\mathcal{Q}}_j^{(l)}$ and $\boldsymbol{\mathcal{Q}}_j^{\mathrm{eff}(l)}$ in Eqs. (90) and (92), we obtain

$$\mathcal{E}_r^* = 1 - \frac{\beta}{\varepsilon_0}\sum_j n_j^{\mathrm{b}}\left[\frac{\mathcal{Q}_j^{\mathrm{eff}}\mathcal{Q}_j - q_j^* q_j}{\kappa^2} + \sum_{l=1}^{\infty}\frac{(-1)^l\kappa^{2(l-1)}(2l+1)^2\, l!}{[(2l+1)!!]^3}\boldsymbol{\mathcal{Q}}_j^{\mathrm{eff}(l)}\bullet\boldsymbol{\mathcal{Q}}_j^{(l)}\right] \tag{B18}$$

where the product $\boldsymbol{\mathcal{Q}}_j^{\mathrm{eff}(l)}\bullet\boldsymbol{\mathcal{Q}}_j^{(l)}$ is independent of ω.

3. Power series expansion in k

By making a Taylor series expansion of the spherical Bessel function in the definitions (B13) and (B14) of $\tilde{\boldsymbol{\rho}}_j^{*(l)}$ and $\tilde{\boldsymbol{\sigma}}_j^{(l)}$, we have (with $\tilde{\mathbf{f}}^{(l)} = \tilde{\boldsymbol{\rho}}_j^{*(l)}$ or $\tilde{\boldsymbol{\sigma}}_j^{(l)}$)

$$\begin{aligned}\tilde{\mathbf{f}}^{(l)}(k,\boldsymbol{\omega}) &\equiv (2l+1)!!\int d\mathbf{r}\,\mathbf{P}_l(\mathbf{r})f(\mathbf{r},\boldsymbol{\omega})\frac{j_l(kr)}{(kr)^l}\\ &= (2l+1)!!\int d\mathbf{r}\,\mathbf{P}_l(\mathbf{r})f(\mathbf{r},\boldsymbol{\omega})\sum_{\nu=0}^{\infty}\frac{(-1)^\nu(kr)^{2\nu}}{\nu!\,2^\nu(2\nu+2l+1)!!}\\ &= \int d\mathbf{r}\,\mathbf{P}_l(\mathbf{r})f(\mathbf{r},\boldsymbol{\omega})\left[1 - \frac{(kr)^2}{1!\,2(2l+3)} + \frac{(kr)^4}{2!\,2^2(2l+3)(2l+5)} - \dots\right].\end{aligned} \tag{B19}$$

From this we can obtain the Taylor series in k of $\tilde{\mathbf{f}}^{(l)}$, for instance,

$$\tilde{f}^{(0)}(k) = \int d\mathbf{r}\, f(\mathbf{r},\boldsymbol{\omega}) - \frac{k^2}{6}\int d\mathbf{r}\, r^2 f(\mathbf{r},\boldsymbol{\omega}) + \frac{k^4}{120}\int d\mathbf{r}\, r^4 f(\mathbf{r},\boldsymbol{\omega}) + \mathcal{O}(k^6)$$

and

$$\tilde{\mathbf{f}}^{(1)}(k,\boldsymbol{\omega}) = \int d\mathbf{r}\, \mathbf{r}\, f(\mathbf{r},\boldsymbol{\omega}) - \frac{k^2}{10}\int d\mathbf{r}\, \mathbf{r}\, r^2 f(\mathbf{r},\boldsymbol{\omega}) + \frac{k^4}{280}\int d\mathbf{r}\, \mathbf{r}\, r^4 f(\mathbf{r},\boldsymbol{\omega}) + \mathcal{O}(k^6).$$

The function $f(\mathbf{r},\boldsymbol{\omega})$ decays fast to zero with r in the cases considered in this paper, so all integrals converge. For the case $f(\mathbf{r},\boldsymbol{\omega}) = \sigma_j(\mathbf{r},\boldsymbol{\omega})$ the first term in the k expansion of $\tilde{\sigma}_j^{(0)}(k)$ is q_j, the charge of a j ion, and the first term in $\tilde{\boldsymbol{\sigma}}_j^{(1)}(k,\boldsymbol{\omega})$ is $\boldsymbol{\mu}_j(\boldsymbol{\omega})$, its dipole moment. Likewise, for $f(\mathbf{r},\boldsymbol{\omega}) = \rho_j^*(\mathbf{r},\boldsymbol{\omega})$ the corresponding terms of $\tilde{\rho}_j^{*(0)}(k)$ and $\tilde{\boldsymbol{\rho}}_j^{(1)}(k,\boldsymbol{\omega})$ are q_j^* and $\boldsymbol{\mu}_j^*(\boldsymbol{\omega})$, respectively; the latter being the dipole moment of the charge distribution ρ_j^*.

By inserting these results in Eq. (B15) we obtain the k expansion of the dielectric function

$$\tilde{\epsilon}(k) = \frac{\beta}{\varepsilon_0 k^2}\sum_j n_j^{\mathrm{b}} q_j q_j^* + b_0^* + b_2^* k^2 + b_4^* k^4 + b_6^* k^6 + \mathcal{O}(k^8), \tag{B20}$$

where we have defined the constants b_ν^* given by

$$b_0^* = 1 + \frac{\beta}{\varepsilon_0}\sum_j n_j^{\mathrm{b}}\left(\frac{1}{3}\boldsymbol{\mu}_j\cdot\boldsymbol{\mu}_j^* - \frac{1}{6}\left[q_j m_j^{*(2)} + q_j^* m_j^{(2)}\right]\right) \tag{B21}$$

$$\begin{aligned} b_2^* = \frac{\beta}{\varepsilon_0}\sum_j n_j^{\mathrm{b}}\Bigg(&\frac{2}{135}\boldsymbol{\Theta}_j \bullet \boldsymbol{\Theta}_j^* - \frac{1}{30}\left[\boldsymbol{\mu}_j\cdot\mathbf{m}_j^{*(1,2)} + \boldsymbol{\mu}_j^*\cdot\mathbf{m}_j^{(1,2)}\right] \\ &+ \frac{1}{120}\left[q_j m_j^{*(4)} + q_j^* m_j^{(4)}\right] + \frac{1}{36} m_j^{(2)} m_j^{*(2)}\Bigg), \end{aligned} \tag{B22}$$

(for b_ν^* with ν even and $\nu \geq 4$, analogous expressions can be obtained in a similar manner). Here we have suppressed $\boldsymbol{\omega}$ for clarity (all terms in b_ν^* are independent of $\boldsymbol{\omega}$) and introduced the moments of order ν of the charge distributions σ_j and ρ_j^*

$$m_j^{(\nu)} = \int d\mathbf{r}\, r^\nu \sigma_j(\mathbf{r},\boldsymbol{\omega})$$

$$m_j^{*(\nu)} = \int d\mathbf{r}\, r^\nu \rho_j^*(\mathbf{r},\boldsymbol{\omega}),$$

the corresponding vectorial moments

$$\mathbf{m}_j^{(1,\nu)}(\boldsymbol{\omega}) = \int d\mathbf{r}\, \mathbf{r}\, r^\nu \sigma_j(\mathbf{r},\boldsymbol{\omega})$$

$$\mathbf{m}_j^{*(1,\nu)}(\boldsymbol{\omega}) = \int d\mathbf{r}\, \mathbf{r}\, r^\nu \rho_j^*(\mathbf{r},\boldsymbol{\omega}),$$

and $\boldsymbol{\Theta}_j^* = \boldsymbol{\Theta}_j^*(\boldsymbol{\omega})$, which is the quadrupole moment of $\rho_j^*(\mathbf{r},\boldsymbol{\omega})$. The coefficients b_4^* and b_6^* contain the octupolar and hexadecapolar moments, respectively, and various other moments like $m_j^{(\nu)}$, $\mathbf{m}_j^{(1,\nu)}$ and higher order tensor moments. The first term in Eq. (B20) is $\tilde{\epsilon}_{\text{sing}}(k)$, so it follows that $\tilde{\epsilon}_{\text{reg}}(k)$ has the Taylor expansion

$$\tilde{\epsilon}_{\text{reg}}(k) = b_0^* + b_2^* k^2 + b_4^* k^4 + b_6^* k^6 + \mathcal{O}(k^8). \tag{B23}$$

This implies that

$$\mathcal{E}_r^* = \tilde{\epsilon}_{\text{reg}}(\mathrm{i}\kappa) = b_0^* - b_2^* \kappa^2 + b_4^* \kappa^4 - b_6^* \kappa^6 + \mathcal{O}(\kappa^8) \tag{B24}$$

and from Eq. (48) we obtain

$$\begin{aligned}\mathcal{E}_r^{\text{eff}} &= \left[\tilde{\epsilon}_{\text{reg}}(k) + \frac{k}{2}\frac{d\tilde{\epsilon}_{\text{reg}}(k)}{dk}\right]_{k=\mathrm{i}\kappa} \\ &= b_0^* - 2b_2^* \kappa^2 + 3b_4^* \kappa^4 - 4b_6^* \kappa^6 + \mathcal{O}(\kappa^8).\end{aligned} \tag{B25}$$

(Incidentally, we note that the second moment $m_j^{(2)}$ that occur in b_0^* would contribute to the quadrupole moment if we had used a definition like $\int d\mathrm{r}\, \mathbf{r}\mathbf{r}\sigma_j(\mathrm{r}, \boldsymbol{\omega})$ for the latter, i.e., a quadrupole moment with nonzero trace. This trace would be equal to the second moment. Likewise, the vectorial moment $\mathbf{m}_j^{(1,2)}$ and the fourth moment $m_j^{(4)}$ that occur in b_2^* would contribute to the octupole and the hexadecapole moments, respectively, if the tensors with nonzero trace were used. In this paper, we use tensors with zero trace throughout.)

4. Expansions of the reciprocal dielectric function

Let us now turn to $1/\tilde{\epsilon}(k)$ as given by Eq. (B3). One can derive the corresponding expansions of this function by following the same procedure as above but with $\tilde{\rho}_j^{\text{tot}}$ instead of $\tilde{\rho}_j^*$. Thereby, one obtains the spherical tensor expansion (cf. Eq. (B9))

$$\frac{1}{\tilde{\epsilon}(k)} = 1 - \frac{4\pi\beta}{\varepsilon_0}\sum_j n_j^{\text{b}} \sum_l \frac{k^{2(l-1)}}{[(2l+1)!!]^2}\tilde{\rho}_{j;l}^{\text{tot}} \star \tilde{\sigma}_{j;l}(k), \tag{B26}$$

with

$$\tilde{\rho}_{j;lm}^{\text{tot}}(k, \boldsymbol{\omega}) = (2l+1)!! \int d\mathbf{r}\, \rho_j^{\text{tot}}(\mathbf{r}, \boldsymbol{\omega})\frac{j_l(kr)}{(kr)^l}\underline{\mathcal{Y}}_{lm}(\mathbf{r}). \tag{B27}$$

The cartesian version of this expansion is (cf. Eq. (B15))

$$\frac{1}{\tilde{\epsilon}(k)} = 1 - \frac{\beta}{\varepsilon_0}\sum_j n_j^{\text{b}} \sum_l \frac{k^{2(l-1)}(2l+1)^2\, l!}{[(2l+1)!!]^3}\tilde{\boldsymbol{\rho}}_j^{\text{tot}(l)} \bullet \tilde{\boldsymbol{\sigma}}_j^{(l)}(k) \tag{B28}$$

with

$$\tilde{\boldsymbol{\rho}}_j^{\text{tot}(l)}(k, \boldsymbol{\omega}) = (2l+1)!! \int d\mathbf{r}\, \mathbf{P}_l(\mathbf{r})\rho_j^{\text{tot}}(\mathbf{r}, \boldsymbol{\omega})\frac{j_l(kr)}{(kr)^l}. \tag{B29}$$

Explicitly, we have

$$\frac{1}{\tilde{\epsilon}(k)} = 1 - \frac{\beta}{\varepsilon_0}\sum_j n_j^{\mathrm{b}}\left[\frac{1}{k^2}\tilde{\rho}_j^{\mathrm{tot}(0)}(k)\tilde{\sigma}_j^{(0)}(k) \right.$$
$$\left. + \frac{1}{3}\tilde{\boldsymbol{\rho}}_j^{\mathrm{tot}(1)}\cdot\tilde{\boldsymbol{\sigma}}_j^{(1)}(k) + \frac{2k^2}{135}\tilde{\boldsymbol{\rho}}_j^{\mathrm{tot}(2)}\bullet\tilde{\boldsymbol{\sigma}}_j^{(2)}(k) + \dots\right], \tag{B30}$$

where the first term in the square bracket stays finite when $k \to 0$ since $\tilde{\rho}_j^{\mathrm{tot}(0)}(0) = 0$.

For an electrolyte, the power series expansion of $1/\tilde{\epsilon}(k)$ in k corresponding to Eq. (B20) is

$$\frac{1}{\tilde{\epsilon}(k)} = b_2k^2 + b_4k^4 + b_6k^6 + \mathcal{O}(k^8), \tag{B31}$$

where the coefficients b_ν can be defined in analogy to the expressions for b_ν^* above as will be discussed below. There is no $1/k^2$ contribution for the reason just given. Since $1/\tilde{\epsilon}(k) \to 0$ when $k \to 0$ for an electrolyte, the constant term corresponding to b_0^* in Eq. (B21) is zero ($b_0 = 0$), which deserves a special comment. Consider (in analogy to Eq. (B21))

$$b_0 = 1 - \frac{\beta}{\varepsilon_0}\sum_j n_j^{\mathrm{b}}\left(\frac{1}{3}\boldsymbol{\mu}_j\cdot\boldsymbol{\mu}_j^{\mathrm{tot}} - \frac{1}{6}\left[q_j m_j^{\mathrm{tot}(2)} + q_j^{\mathrm{tot}} m_j^{(2)}\right]\right) \tag{B32}$$

where q_j^{tot} and $\boldsymbol{\mu}_j^{\mathrm{tot}}$ are the total charge and the dipole moment, respectively, of $\rho_j^{\mathrm{tot}}(\mathbf{r},\boldsymbol{\omega})$ and we have defined the moments

$$m_j^{\mathrm{tot}(\nu)} = \int d\mathbf{r}\, r^\nu \rho_j^{\mathrm{tot}}(\mathbf{r},\boldsymbol{\omega}).$$

Now, not only $q_j^{\mathrm{tot}} = 0$ but also the dipole moment, $\boldsymbol{\mu}_j^{\mathrm{tot}} = 0$, and all corresponding multipole moments are zero in an electrolyte, for example the quadrupole moment $\boldsymbol{\Theta}_j^{\mathrm{tot}}$ of $\rho_j^{\mathrm{tot}}(\mathbf{r},\boldsymbol{\omega})$. This is a consequence of the perfect screening in electrolytes and has been rigorously proven for systems with ions and dipolar particles.[73] Perfect screening also lies behind the divergence of $\tilde{\epsilon}(k)$ when $k \to 0$ and the second moment condition (cf. Eq. (A2))

$$\beta\sum_j n_j^{\mathrm{b}} q_j m_j^{\mathrm{tot}(2)} = -6\varepsilon_0, \tag{B33}$$

which also has been proven rigorously for systems with ions and dipolar particles.[74] Indeed, one obtains $b_0 = 0$ by inserting Eq. (B33), $q_j^{\mathrm{tot}} = 0$ and $\boldsymbol{\mu}_j^{\mathrm{tot}} = 0$ in expression (B32).

In analogy to Eq. (B22) we have

$$b_2 = -\frac{\beta}{\varepsilon_0}\sum_j n_j^{\mathrm{b}}\left(\frac{2}{135}\boldsymbol{\Theta}_j\bullet\boldsymbol{\Theta}_j^{\mathrm{tot}} - \frac{1}{30}\left[\boldsymbol{\mu}_j\cdot\mathbf{m}_j^{\mathrm{tot}(1,2)} + \boldsymbol{\mu}_j^{\mathrm{tot}}\cdot\mathbf{m}_j^{(1,2)}\right]\right.$$
$$\left. + \frac{1}{120}\left[q_j m_j^{\mathrm{tot}(4)} + q_j^{\mathrm{tot}} m_j^{(4)}\right] + \frac{1}{36}m_j^{(2)}m_j^{\mathrm{tot}(2)}\right), \tag{B34}$$

where

$$\mathbf{m}_j^{\mathrm{tot}(1,\nu)}(\boldsymbol{\omega}) = \int d\mathbf{r}\,\mathbf{r}\,r^{\nu}\rho_j^{\mathrm{tot}}(\mathbf{r},\boldsymbol{\omega}).$$

Since q_j^{tot}, $\boldsymbol{\mu}_j^{\mathrm{tot}}$ and $\boldsymbol{\Theta}_j^{\mathrm{tot}}$ are zero, Eq. (B34) can be simplified to

$$b_2 = \frac{\beta}{\varepsilon_0}\sum_j n_j^{\mathrm{b}}\left[\frac{1}{30}\boldsymbol{\mu}_j \cdot \mathbf{m}_j^{\mathrm{tot}(1,2)} - \frac{1}{120}q_j m_j^{\mathrm{tot}(4)} - \frac{1}{36}m_j^{(2)}m_j^{\mathrm{tot}(2)}\right] \tag{B35}$$

for an electrolyte. Since we must have

$$\begin{aligned}\tilde{\epsilon}(k) &= \frac{\beta}{\varepsilon_0 k^2}\sum_j n_j^{\mathrm{b}} q_j q_j^* + b_0^* + b_2^* k^2 + b_4^* k^4 + b_6^* k^6 + \dots \\ &= \frac{1}{b_2 k^2 + b_4 k^4 + b_6 k^6 + \dots}\end{aligned}$$

it follows that

$$\frac{\beta}{\varepsilon_0}\sum_j n_j^{\mathrm{b}} q_j q_j^* = \frac{1}{b_2}, \tag{B36}$$

which for the case of spherical ions with central point charges agrees with Eq. (A9) since $\boldsymbol{\mu}_j = 0$ and $m_j^{(2)} = 0$ in that case, so Eq. (B35) reduces to Eq. (A8). Furthermore, it follows that b_ν^* can be expressed in terms $b_{\nu'}$ for various ν', for instance $b_0^* = -b_4/(b_2)^2$.

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[44] The following arguments are based on results for binary electrolytes in Ref. [36] (where different notation is used). The functions $w_{ij}(r)$ and $h_{ij}(r) = \exp[-\beta w_{ij}(r)] - 1 \sim -\beta w_{ij}(r)$ decay for large r in a plain exponential or exponentially damped oscillatory manner when $\tilde{h}_{ij}(k)$ has a pole in complex Fourier space (the leading term in the decay corresponds to the pole closest to the real axis). Consider the function $\tilde{h}_{ij}^{*}(k) = \tilde{h}_{ij}(k) + \beta \tilde{w}_{ij}^{\mathrm{el}}(k)$. The pole of $\tilde{h}_{ij}(k)$ is either a pole of $\tilde{h}_{ij}^{*}(k)$ or $\tilde{w}_{ij}^{\mathrm{el}}(k) \equiv \tilde{\rho}_i^{*}(k)\tilde{\phi}_{\mathrm{Coul}}^{*}(k)\tilde{\rho}_j^{*}(k)$. The function $\tilde{w}_{ij}^{\mathrm{el}}(k)$ has a pole at $k = \mathrm{i}\kappa$ since $\tilde{\phi}_{\mathrm{Coul}}^{*}(k) = 1/[\varepsilon_0 k^2 \tilde{\epsilon}(k)]$ and $\tilde{\epsilon}(\mathrm{i}\kappa) = 0$. It is shown in Ref. [36] that $\tilde{h}_{ij}^{*}(k)$ cannot have a pole at $k = \mathrm{i}\kappa$ (apart from exceptional points in parameter space where the leading term

of the charge-charge correlations fortuitously vanish, e.g. a critical point). In fact, we have $\tilde{\rho}_i^*(k) = q_i + \sum_j q_j n_j^{\mathrm{b}} \tilde{h}_{ij}^*(k)$ and it is shown in Ref. [36] that any pole of $\tilde{h}_{ij}^*(k)$ is cancelled in the combination $\tilde{h}_{ij}^*(k) - \beta \tilde{w}_{ij}^{\mathrm{el}}(k)$, so the poles of $\tilde{h}_{ij}(k)$ cannot originate from $\tilde{h}_{ij}^*(k)$. Therefore, the leading pole of $\tilde{h}_{ij}(k)$ and hence that of $\tilde{w}_{ij}(k)$ originates from $\tilde{w}_{ij}^{\mathrm{el}}(k)$ and occurs at $k = \mathrm{i}\kappa$. It follows that $w_{ij}(r)$ and $\phi_{\mathrm{Coul}}^*(r)$ decays in the same fashion [this is true even if $h_{ij}^*(r)$ and $\rho_i^*(r)$ decay slower than $\phi_{\mathrm{Coul}}^*(r)$, but we do not have $w_{ij}(r) \sim w_{ij}^{\mathrm{el}}(r)$ since w_{ij}^{el} decays slower than w_{ij} in such cases]. An exception to these results are electrolytes where anions and cations are identical apart from the sign of charge (like the restricted primitive model); the "symmetric electrolyte" case in Ref. [36]. Then the charge-density correlations are identically zero for symmetry reasons and it is possible that $w_{ij}(r)$ decays slower than $\phi_{\mathrm{Coul}}^*(r)$. This occurs when density-density correlations from the effects of packing of spheres is more important than electrostatics.[36, 54]

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[46] Equation (39) with Eq. (13) inserted can be expressed as $\kappa^2 = \beta \sum_j n_j^{\mathrm{b}} q_j q_j^{\mathrm{eff}} / \varepsilon_0$, where $q_j^{\mathrm{eff}} = \int d\mathbf{r} \rho_j^*(r) \sinh(\kappa r)/(\kappa r)$, see Refs. [34, 35] (where q_j^{eff} denoted q_j^*, which is different from q_j^* in the current paper). This appealing expression for κ^2 is, however, only applicable for spherical ions and is replaced by Eq. (79) for the nonspherical case. In contrast to this, Eq. (3) is valid in general as demonstrated in Section III. Note that q_j^{eff} for spherical ions is in general *not* equal to $q_j^*/\mathcal{E}_r^*$ despite that the formulas for κ^2 may appear to indicate that they should be equal.

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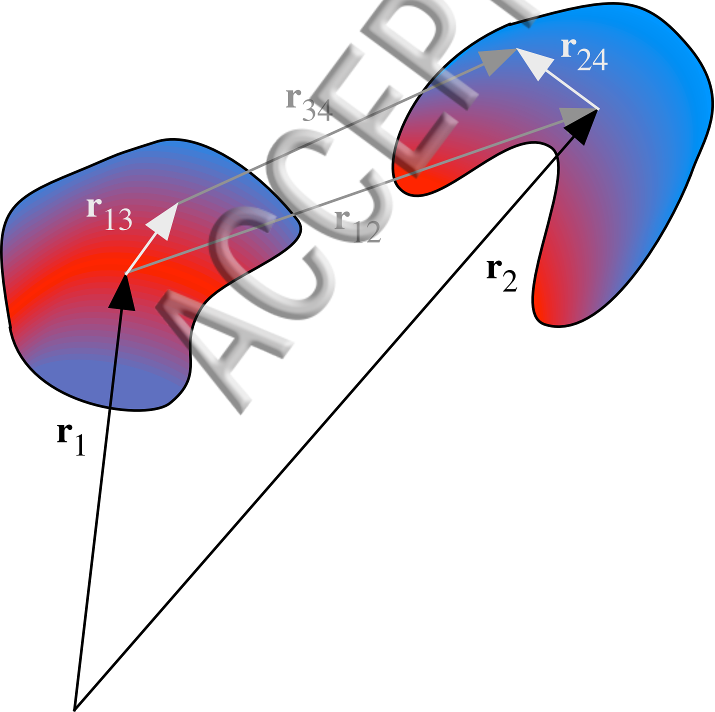
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