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Yukawa multipole electrostatics and nontrivial coupling between electrostatic and dispersion interactions in electrolytes

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Abstract

An exact treatment of screened electrostatics in electrolyte solutions is presented. In electrolytes the anisotropy of the exponentially decaying electrostatic potential from a molecule extends to the far field region. The full directional dependence of the electrostatic potential from a charged or uncharged molecule remains in the longest range tail (i.e. from all multipole moments). In particular, the range of the potential from an ion and that from an electroneutral polar particle is exactly the same in general. This is in contrast to the case in vacuum or pure polar liquids, where the potential from a single charge is longer ranged than that from a dipole, which is, itself, longer ranged than the one from a quadrupole etc. The orientational dependence of the exponentially screened electrostatic interaction between two molecules in electrolytes is therefore rather complex even at long distances. These facts are formalized in Yukawa multipole expansions of the electrostatic potential and the pair interaction free energy based on the Yukawa function family $\exp(-\kappa r)/r^m$, where r is the distance, κ is a decay parameter and m is a positive integer. The expansion is formally exact for electrolytes with molecular solvent and in the primitive model, provided the non-Coulombic interactions between the particles are sufficiently short ranged. The results can also be applied in the Poisson–Boltzmann approximation. Differences and similarities to the ordinary multipole expansion of electrostatics are pointed out.

On the other hand, when the non-Coulombic interactions between the constituent particles of the electrolyte solution contain a dispersion $1/r^6$ potential, the electrostatic potential from a molecule decays like a power law for long distances rather than as a Yukawa function. This is due to nontrivial coupling between the electrostatic and dispersion interactions. There remains an exponentially decaying component in the electrostatic potential, but it becomes oscillatory in the presence of the dispersion interactions. For weak dispersion forces and low electrolyte concentrations, the wavelength is, however, long compared to the decay length of the exponential decay. In other cases the qualitative behaviour may be substantially different from the conventional picture. The Green function for the electrostatic potential (the ‘screened Coulomb potential’) in simple electrolytes ultimately decays like const/r^6 for large r , where the constant prefactor depends on the ratio between the strength of the dispersion forces and the square of the average ionic charge, $(q_+ + |q_-|)/2$.

1. Introduction

Screening of electrostatic interactions is a prominent and important property of electrolytes and is a central concept in our understanding of systems like bulk salt solutions, colloidal

dispersions, polyelectrolytes and macromolecular solutions. Such systems are of importance in, for example, biosciences, soft matter physics, soil science and surface and colloid chemistry. Often, the term ‘screened Coulomb potential’ is equated with the potential from a charge in an electrolyte

as predicted by the Debye–Hückel theory [1] for electrolyte solutions. This potential has the form of a Yukawa function $\exp(-\kappa_D r)/r$ for all distances r , where the decay length $1/\kappa_D$ equals the Debye length. In the application of this potential to calculate interactions between charged particles or functional groups, it is common to use the actual charges of the various entities to obtain the electrostatic interaction energy. The results of the Debye–Hückel theory are, however, only valid for sufficiently dilute solutions, where one can neglect ion–ion correlations (including the effects of finite ion sizes) among the ions in the ion atmosphere surrounding each ion. The Debye–Hückel theory is based on the Poisson–Boltzmann (PB) mean field approximation, where such correlations are ignored. The PB approximation is also the basis for the Gouy–Chapman [2, 3] theory for electric double layers and the related Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [4, 5] of colloidal particle interactions. In the latter theory, the forces between the particles consist of the sum of van der Waals (vdW) and electric double layer interactions, which are assumed to be independent of each other and additive.

The PB theory is an approximation within the primitive model of electrolyte solutions where the ions are modelled as charged hard spheres and solvent is treated as a dielectric continuum solely characterized by its dielectric constant (relative permittivity) ϵ_r . When many-body ionic correlations are important the screened Coulomb potential is no longer a simple Yukawa function, but provided the electrolyte concentration is not too high the potential decays like such a function for large r within the primitive model [6]. This also holds in electrolyte solution models with discrete solvent molecules [7]. The Yukawa function decay of the electrostatic potential in electrolytes has consequences that until recently have been largely ignored, namely the anisotropy of the potential from a molecule in the far field region. This feature has been found in linearized PB approaches [8–11] and in exact statistical mechanics treatment of electrolytes with molecular solvent [12].

The exponential decay of the electrostatic interactions for large r holds provided the nonelectrostatic interactions between all particles in the solution are sufficiently short ranged. This excludes systems with vdW interactions between the particles. The screened electrostatic interactions and vdW interactions are not independent of each other and additive as assumed in the DLVO theory. Instead, they are coupled so that the electrostatics changes the effects of the vdW interactions and vice versa. The static (zero frequency) part of the vdW interaction is screened by the electrolyte [13] and becomes exponentially short ranged. This is not the case for the high frequency part, which gives an r^{-6} interaction between the particles for large r (or r^{-7} when retardation effects are included). Such power law interactions affect the electrostatic interactions and make the electrostatic potential decay like a power law rather than exponentially for large r ; this holds both in mean field PB-like treatment [14] and in exact statistical mechanics analysis [15, 16]. Furthermore, it has been suggested that London-type dispersion interactions between ions and between ions and other particles may play a role in determining the ion

specificity of a range of phenomena related to charged particles in electrolytes [17]. These matters have been explored in a number of recent publications; see for example [14, 18–21]. Thus qualitative as well as quantitative effects of ion–ion and ion–macroparticle dispersion interactions are of great interest for both fundamental and applied research.

In the present work we shall primarily explore consequences of Yukawa-type screening for electrolyte systems, but also investigate effects of nonelectrostatic power law interactions in simple electrolytes. For the first topic we will build on and expand the findings of our previous work [7, 12], to which we refer for mathematical details and background material. Thereby, our aim is to present the results of the analysis in a manner that suits nonspecialists in liquid state theory (for completeness, we have also inserted some more technical comments which can be skipped over in a first reading). Important issues include the concepts of effective charge, effective dipole and higher order multipoles and investigations of the long distance features of the screened electrostatic potential from a molecule and of the interaction free energy between molecules in electrolytes with molecular solvent. Finally, we shall investigate the behaviour of the screened Coulomb potential in simple electrolytes with dispersion r^{-6} interactions between the ions. This is based on the findings in [15, 16], which we formulate in the perspective of the general theme of the present work.

Unless otherwise explicitly stated, the statistical mechanical analysis presented in this paper is exact (no approximations made) for given pair interaction potentials between the particles (i.e. for a given Hamiltonian). We shall consider electrostatic potential from and interactions between particles present in (or immersed in) homogeneous, isotropic bulk systems at equilibrium. The results are valid provided the electrolyte concentration is not too high (what is too high depends on the system), and we will assume that the system is not close to criticality.

We will treat both rigid and flexible molecules. For rigid molecules their relative positions and orientations are relevant. If the molecules are flexible we consider the orientations for all possible conformations. For simplicity, whenever we in the following only say ‘orientation’ of a molecule, we will implicitly mean ‘conformation and orientation’ when the molecule is flexible. The molecules and other particles in the system can have any size, shape and internal charge density distribution (unless otherwise explicitly stated). We will assume that the solvent consists of electroneutral molecules that (usually) are polar. The solutes can have a net charge or be electroneutral. The charged solutes can be simple ions (i.e. small, spherical particles with a charge at their centre), more complex ions with various polar and nonpolar groups, macroions and/or colloidal particles. In the primitive model the solvent is replaced by a dielectric continuum and the ions are charged hard spheres.

In the general, exact case we treat all particles of the system on the same fundamental level for an infinite system at equilibrium. Therefore, the average density around a fixed particle is the same as when the particle is free to move in the system, provided that the density in the latter case is recorded

in the molecule-fixed frame of reference, i.e. we ‘sit’ on the particle, follow its motion and investigate the surrounding density. This is a property of classical equilibrium statistical mechanics, where the momentum degrees of freedom are decoupled from the positional ones. Everything we say here about an immersed, fixed particle in the exact case is true also for the same kind of particle present in the system and free to move.

The paper is organized as follows. In the next section we discuss polarization of bulk electrolyte solutions in various cases and give a general definition of the unit screened Coulomb potential from several equivalent perspectives. Then we present the results of a general treatment of electrostatic potential and intermolecular screened electrostatic interactions in electrolytes with molecular solvent as well as in the primitive model. A simple illustrative example of screened electrostatic potential from a dipole is given, which illuminates some prominent features of the general theory. A key concept in the theory is charge density renormalization of molecules, which is motivated and defined in a physical manner. We give exact expressions for the long-distance asymptotic behaviour of screened electrostatic potential and intermolecular interactions and discuss their implications. In the final part of the paper we treat simple electrolytes with intermolecular dispersion and other power law interactions. We examine the long-range behaviour of various correlation functions and the screened Coulomb potential. The changes imposed on the exponential part of the screening by the dispersion interactions are also discussed. Finally, the main results of the paper are summarized (an overview of the decay behaviour of the electrostatic potential is shown in table 1, which can be useful to examine while reading the paper).

2. Polarization charge density and screened Coulomb potential

A bulk electrolyte solution exposed to an external electrostatic potential $\Psi^{\text{Ext}}(\mathbf{r}_1)$ from some source charges immersed in the solution acquires a polarization charge density $\rho^{\text{pol}}(\mathbf{r}_2)$, which originates from changes in the spatial distributions and orientations of solvent molecules and dissolved ions (we use the notation $\mathbf{r}_\alpha = (x_\alpha, y_\alpha, z_\alpha)$). The resulting total electrostatic potential $\Psi(\mathbf{r})$ from the source charges and the polarization charge density is

$$\Psi(\mathbf{r}_1) = \Psi^{\text{Ext}}(\mathbf{r}_1) + \int d\mathbf{r}_2 \rho^{\text{pol}}(\mathbf{r}_2) \phi_{\text{Coul}}(r_{21}) \quad (1)$$

where

$$\phi_{\text{Coul}}(r) = \frac{1}{4\pi\epsilon_0 r} \quad (2)$$

is the Coulomb potential in vacuum, ϵ_0 is the vacuum permittivity, $r_{21} = |\mathbf{r}_{21}|$ and $\mathbf{r}_{21} = \mathbf{r}_1 - \mathbf{r}_2$. For weak electrostatic fields the polarization charge density can be expressed in linear response theory as

$$\rho^{\text{pol}}(\mathbf{r}_2) = \int d\mathbf{r}_3 \Psi^{\text{Ext}}(\mathbf{r}_3) \chi(r_{32}) = \int d\mathbf{r}_3 \Psi(\mathbf{r}_3) \chi^0(r_{32}) \quad (3)$$

(linear response)

where $\chi(r)$ and $\chi^0(r)$ are the polarization response functions for the external and total potentials, respectively. These functions can be written in terms of the pair correlation functions of the unperturbed bulk electrolyte solution (or more specifically, in terms of the charge–charge correlation function). In Fourier space the relationship between Ψ and Ψ^{Ext} can be written as

$$\tilde{\Psi}(\mathbf{k}) = \frac{\tilde{\Psi}^{\text{Ext}}(\mathbf{k})}{\tilde{\epsilon}(k)} \quad (\text{linear response}) \quad (4)$$

where

$$\tilde{\epsilon}(k) = [1 + \tilde{\chi}(k)\tilde{\phi}_{\text{Coul}}(k)]^{-1} = 1 - \tilde{\chi}^0(k)\tilde{\phi}_{\text{Coul}}(k) \quad (5)$$

is the (static longitudinal) dielectric function and $\tilde{\phi}_{\text{Coul}}(k) = 1/(\epsilon_0 k^2)$ is the Fourier transform of the Coulomb potential. For pure solvent (zero electrolyte concentration) the dielectric function $\tilde{\epsilon}(k)$ approaches the dielectric constant ϵ_r of the solvent when $k \rightarrow 0$ (i.e. infinite wavelength, corresponding to the response to a uniform applied electrostatic field). In the presence of electrolyte $\tilde{\epsilon}(k)$ diverges like k^{-2} when $k \rightarrow 0$, which is a consequence of the electrolyte solution being a conductor.

For a bulk solution the Green’s function for spatial propagation of total electrostatic potential between \mathbf{r}_1 and \mathbf{r}_2 in the weak field limit, $\phi_{\text{Coul}}^0(\mathbf{r}_2, \mathbf{r}_1) = \phi_{\text{Coul}}^0(r_{12})$, satisfies the Poisson equation

$$-\epsilon_0 \nabla^2 \phi_{\text{Coul}}^0(r_{12}) = \int d\mathbf{r}_3 \phi_{\text{Coul}}^0(r_{13}) \chi^0(r_{32}) + \delta^{(3)}(r_{12}), \quad (6)$$

where the first term in the right hand side (rhs) is the polarization charge density from ϕ_{Coul}^0 , cf equation (3), and $\delta^{(3)}(r)$ is the three-dimensional Dirac function (which constitutes the unit source charge of ϕ_{Coul}^0). Equivalently, ϕ_{Coul}^0 is in Fourier space given by

$$\tilde{\phi}_{\text{Coul}}^0(k) = \frac{\tilde{\phi}_{\text{Coul}}(k)}{\tilde{\epsilon}(k)}, \quad (7)$$

which according to equation (4) gives the total potential $\phi_{\text{Coul}}^0(r)$ in the electrolyte solution that corresponds to an external Coulomb potential given by $\phi_{\text{Coul}}(r) = 1/(4\pi\epsilon_0 r)$. The physical interpretation of $\phi_{\text{Coul}}^0(r)$ is that it constitutes the (normalized) *screened Coulomb potential* from a point charge q in the weak field limit, i.e.

$$\phi_{\text{Coul}}^0(r) = \lim_{q \rightarrow 0} \frac{\psi_{[q]}(r)}{q}, \quad (8)$$

where $\psi_{[q]}(r)$ is the total electrostatic potential at distance r from a point charge q (a hypothetical test charge). Thus, the potential from a point charge q immersed in an electrolyte solution approaches $q\phi_{\text{Coul}}^0(r)$ in the limit $q \rightarrow 0$. Note that the three definitions of the screened Coulomb potential ϕ_{Coul}^0 in equations (6)–(8) are mathematically equivalent and define $\phi_{\text{Coul}}^0(r)$ for all r . We shall denote ϕ_{Coul}^0 as the *unit screened Coulomb potential*.

The electrostatic potential from a *finite* point charge q immersed in the electrolyte solution is not equal to $q\phi_{\text{Coul}}^0(r)$

Table 1. The behaviour of the electrostatic potential from a particle in the various cases covered in this paper for low to moderate electrolyte concentrations. In the table ‘=’ means that the expression holds for all r , while ‘~’ means that the expression shows the asymptotic decay for large r . The ordinary (unscreened) Coulomb potential is shown in the second column (the case of vacuum), while the screened Coulomb potential is shown for the other cases. The relative permittivity (dielectric constant) of the pure solvent is ϵ_r . The quantity E_r is the effective permittivity of the electrolyte solution (defined in equation (20)). The bare net charge of a particle of species i is denoted q_i , the dipole moment μ_i and the quadrupole moment Θ_i . The corresponding effective quantities, defined in equations (36)–(38), are denoted q_i^0 , μ_i^0 and Θ_i^0 . The Debye screening parameter is denoted κ_D (the Debye length is κ_D^{-1}), while κ is the actual screening parameter of the electrolyte solution ($\kappa \neq \kappa_D$). Except for the last two rows, the results are strictly valid only in the absence of dispersion interactions (and other power law nonelectrostatic interactions) between the particles. In the last two rows, the coefficients L_{QQ} and Λ_{QN} (defined in equations (64) and (60), respectively) depend on the strengths of both the dispersion and electrostatic interactions.

	Electrostatic potential		
	In vacuum	In pure solvent	In electrolyte solution
<i>Poisson–Boltzmann approximation</i>			
Unit (screened) Coulomb potential	$= \frac{1}{4\pi\epsilon_0 r}$	$= \frac{1}{4\pi\epsilon_r\epsilon_0 r}$ ^a	$= \frac{e^{-\kappa_D r}}{4\pi\epsilon_r\epsilon_0 r}$
Potential $\psi_i(r)$ from a simple ion	$= \frac{q_i}{4\pi\epsilon_0 r}$	$= \frac{q_i}{4\pi\epsilon_r\epsilon_0 r}$ ^b	$\sim \frac{q_i^0 e^{-\kappa_D r}}{4\pi\epsilon_r\epsilon_0 r}$
<i>Primitive model, exact results</i>			
Unit (screened) Coulomb potential	$= \frac{1}{4\pi\epsilon_0 r}$	$= \frac{1}{4\pi\epsilon_r\epsilon_0 r}$ ^a	$\sim \frac{e^{-\kappa r}}{4\pi E_r\epsilon_0 r}$
Potential $\psi_i(r)$ from a simple ion	$= \frac{q_i}{4\pi\epsilon_0 r}$	$= \frac{q_i}{4\pi\epsilon_r\epsilon_0 r}$ ^b	$\sim \frac{q_i^0 e^{-\kappa r}}{4\pi E_r\epsilon_0 r}$
<i>With molecular solvent, exact results</i>			
Unit (screened) Coulomb potential	$= \frac{1}{4\pi\epsilon_0 r}$	$\sim \frac{1}{4\pi\epsilon_r\epsilon_0 r}$	$\sim \frac{e^{-\kappa r}}{4\pi E_r\epsilon_0 r}$
Potential $\psi_i(r)$ from a simple ion	$= \frac{q_i}{4\pi\epsilon_0 r}$	$\sim \frac{q_i}{4\pi\epsilon_r\epsilon_0 r}$ ^b	$\sim \frac{q_i^0 e^{-\kappa r}}{4\pi E_r\epsilon_0 r}$
Potential $\psi_i(\mathbf{r})$ from a molecule ^c	$\sim \frac{q_i}{4\pi\epsilon_0 r}$ $+ \frac{\mu_i \cdot \hat{\mathbf{r}}}{4\pi\epsilon_0 r^2} + \dots$	$\sim \frac{q_i}{4\pi\epsilon_r\epsilon_0 r}$ $+ \frac{\mu_i^0 \cdot \hat{\mathbf{r}}}{4\pi\epsilon_r\epsilon_0 r^2} + \dots$	$\sim \frac{[q_i^0 + \kappa\mu_i^0 \cdot \hat{\mathbf{r}} + \frac{\kappa^2}{3}\Theta_i^0 \cdot \hat{\mathbf{r}}\hat{\mathbf{r}} + \dots]e^{-\kappa r}}{4\pi E_r\epsilon_0 r}$ $+ \frac{[\mu_i^0 \cdot \hat{\mathbf{r}} + \kappa\Theta_i^0 \cdot \hat{\mathbf{r}}\hat{\mathbf{r}} + \dots]e^{-\kappa r}}{4\pi E_r\epsilon_0 r^2} + \dots$
<i>With dispersion interactions between ions, exact results</i>			
Unit screened Coulomb potential			$\sim -\frac{L_{QQ}}{r^6}$
Potential $\psi_i(r)$ from a simple ion			Also oscillatory exponential terms $\sim \frac{nq\Lambda_{QN}}{\epsilon_r\epsilon_0 r^6}$
			Also oscillatory exponential terms

^a Basic assumption in the primitive model where the solvent is treated as a dielectric continuum.

^b Potential from a single ion immersed in pure solvent.

^c The analogous result holds for an electrolyte solution treated in the primitive model (both as an exact result and in the Poisson–Boltzmann approximation), but then for the potential from a single molecule immersed in the solution.

since the polarization response near the charge is nonlinear. Thus the unit screened Coulomb potential is not the potential from a unit point charge since such a charge is not small. For long distances from the charge where the weak field limit applies, the potential from a point charge q is usually proportional to $\phi_{\text{Coul}}^0(r)$ and asymptotically we have $\psi_{[q]}(r) \sim q^0 \phi_{\text{Coul}}^0(r)$ when $r \rightarrow \infty$, where the prefactor q^0 in general is different from q . (In cases where $\phi_{\text{Coul}}^0(r)$ is oscillatory, e.g. for high electrostatic coupling in the electrolyte, the phase of $\psi_{[q]}(r)$ is generally different from that of $\phi_{\text{Coul}}^0(r)$ but the decay is otherwise the same for large r .)

Likewise, a simple spherical ion of species j with charge q_j in the electrolyte solution gives rise in general to a total electrostatic potential $\psi_j(r)$ which is proportional to $\phi_{\text{Coul}}^0(r)$ for large r , i.e.

$$\psi_j(r) \sim q_j^0 \phi_{\text{Coul}}^0(r) \quad (9)$$

when $r \rightarrow \infty$ (the same comment about the phase applies as for $\psi_{[q]}(r)$). The prefactor q_j^0 can be interpreted as the effective charge of the j ion in solution. The value of the effective charge depends on the spatial distributions and orientations of the particles in the solution around the ion. The

polarization of the solution around the ion originates not only from electrostatic interactions, but all kinds of interactions that affect the relative distribution of positive and negative charges. Exceptions from equation (9) occur when the leading term in $\phi_{\text{Coul}}^0(r)$ for large r for some reason is cancelled in $\psi_j(r)$ and a higher order term gives the leading decay of $\psi_j(r)$. An example is a state of the system where the effective charge of the i ion is zero.

Consider now any particle of species i (an ‘ i particle’) in an electrolyte solution. It can have any size, shape and internal charge distribution. If the particle is a flexible molecule we consider the molecule in a certain, but arbitrary conformation. Let us place the origin of the coordinate system at the centre of mass of the particle. We shall henceforth refer to this particle as the ‘central’ one. The internal charge density distribution of the central i particle is denoted $\sigma_i(\mathbf{r}; \omega)$, where the symbol ω denotes the orientation of the particle relative to the coordinate system and, when the particle is a flexible molecule, ω also contains information about conformation of the molecule. The bare (net) charge q_i and dipole moment μ_i of the particle are

given by

$$\begin{aligned} q_i &= \int d\mathbf{s} \sigma_i(\mathbf{s}; \omega) \\ \boldsymbol{\mu}_i(\omega) &= \int d\mathbf{s} \sigma_i(\mathbf{s}; \omega) \mathbf{s} \end{aligned} \quad (10)$$

and analogously for the quadrupole and higher moments.

The average charge density distribution at position \mathbf{r} in the solution around the central i particle is denoted $\rho_i^{\text{ex}}(\mathbf{r}; \omega)$ (the superscript ex = excess stands for ‘in excess of the internal density’). This charge density can be calculated from the pair distribution functions between species i and all species present in the electrolyte solution. It constitutes the charge density of the ‘ion and solvent cloud’ that surrounds the particle. The total charge density distribution of the particle and its surrounding cloud is

$$\rho_i(\mathbf{r}; \omega) = \sigma_i(\mathbf{r}; \omega) + \rho_i^{\text{ex}}(\mathbf{r}; \omega). \quad (11)$$

The condition of local electroneutrality dictates that $\int d\mathbf{u} \rho_i(\mathbf{u}; \omega) = 0$. Note that ρ_i^{ex} contains both the linear and nonlinear electrostatic polarization response of the electrolyte due to the internal charges of the particle as well as the polarization response to all other interactions with the particle. The charge density $\rho_i^{\text{ex}}(\mathbf{r}; \omega)$ is in general nonzero even when $\sigma_i(\mathbf{r}; \omega) = 0$ and, for example, even when the nonelectrostatic interaction with the particle is just a hard core exclusion potential. In fact, any asymmetry between positive and negative charges for the ions and solvent molecules in the electrolyte solution gives rise to a nonzero ρ_i^{ex} even when the particle is an uncharged hard sphere.

The total electrostatic potential ψ_i from an i particle is given by Coulomb’s law as

$$\psi_i(\mathbf{r}_{12}; \omega) = \int d\mathbf{r}_3 \rho_i(\mathbf{r}_{13}; \omega) \phi_{\text{Coul}}(r_{32}). \quad (12)$$

It depends on the direction of \mathbf{r}_{12} for a fixed orientation ω of the particle. A major task in this paper is to describe properties of this potential in various cases. (Note that the potential $\psi_{[q]}(r)$ above is a special case where σ corresponds to a point charge at the origin.)

In pure solvent the unit screened Coulomb potential decays for large r like [22, 23]

$$\phi_{\text{Coul}}^0(r) \sim \frac{\phi_{\text{Coul}}(r)}{\epsilon_r} = \frac{1}{4\pi\epsilon_r\epsilon_0 r} \quad (\text{pure solvent}) \quad (13)$$

where ϵ_r is the dielectric constant of the solvent, $\epsilon_r = \tilde{\epsilon}(0)$. For small r the functional dependence is more complicated and depends on the values of $\tilde{\epsilon}(k)$ for nonzero k , cf equation (7). The total electrostatic potential from a single i particle immersed in pure solvent decays like

$$\psi_i(\mathbf{r}; \omega) \sim q_i \phi_{\text{Coul}}^0(r) = \frac{q_i}{4\pi\epsilon_r\epsilon_0 r} \quad (\text{single particle in pure solvent}) \quad (14)$$

when $r \rightarrow \infty$. The effective charge of the particle is hence equal to the bare charge in this case. The oriented solvent molecules that surround the particle do not contribute to the effective charge (i.e. the effective *net* charge) since they are electroneutral. They only contribute to dielectric screening of

charges at long distances via the dielectric constant, i.e. the linear part of the polarization response contained in ϕ_{Coul}^0 . Note that equation (14) holds irrespective of how strongly the solvent molecules are oriented near the particle, i.e. even if nonlinear polarization effects like dielectric saturation are important there. The nonlinear response does, however, contribute to an effective dipole moment of the particle, which in general is not equal to the bare $\boldsymbol{\mu}_i$. The dipolar potential decays like r^{-2} and does not contribute to the leading term shown in equation (14). The latter therefore does not depend on the direction of \mathbf{r} . The potentials from the corresponding higher multipoles of the particle and the induced distribution do not contribute either to the leading term. These potentials decay even faster, exactly like in the multipole expansion of the potential from a charge distribution in vacuum.

In electrolyte solutions the corresponding results are, as we shall see in the remainder of this paper, entirely different. Furthermore, the nature of the short-ranged nonelectrostatic part of the interactions can make a difference in the qualitative behaviour of the electrostatic potential. If the nonelectrostatic interactions decay like a power law, e.g. a dispersion r^{-6} potential, we have one behaviour, and if they decay faster than a power law, e.g. an exponentially decaying or a finite-range potential (like a hard core or square well potential), we have a different behaviour.

3. Electrolytes with very short-ranged nonelectrostatic part of the intermolecular interactions

We start by considering model electrolytes where all molecules in the solution interact with electrostatic and short-ranged pair interactions, where the latter decay with r faster than any power law. The simplest example is the primitive model of electrolytes. More elaborate examples are ‘civilized’ model electrolytes where the solvent molecules are explicitly included, e.g. as hard bodies with electric dipoles and/or multipoles. The treatment also includes any model of charged and uncharged molecules with arbitrary internal charge distributions and of any size and shape, provided there are no nonelectrostatic interactions that decay for large separations like a power law. This includes finite range potentials and exponentially decaying potentials, provided the decay length is shorter than that of the pair distribution functions. All models with, for example, Lennard-Jones potentials are however *excluded* here. Their treatment is postponed to section 4.

Our analysis of electrostatic interactions in [7, 12], on which the present study is built, was restricted to rigid molecules with any size, shape and internal charge distribution. We here extend the analysis to flexible molecules. All results derived in [7, 12] for rigid molecules are also valid for flexible ones provided the following changes are made: a flexible molecule in a particular conformation is formally regarded as a separate rigid species with a certain concentration. The same molecule in different conformations (different conformers) is thereby regarded as a mixture of different rigid species with different concentrations. The condition that makes all these

species correspond to the same actual molecule is that the concentration of each conformer is such that the chemical potential of all conformers is the same. The intramolecular interaction energy is included in the chemical potential. Since the results in our previous work are valid for mixtures of rigid particles with any shape and internal charge distribution, the only change necessary is to increase the number of species and have appropriate concentrations. (We use here the symbol ω to denote the orientation of a rigid molecule relative to the laboratory frame and to denote the conformer and its orientation for a flexible molecule. By using the analogous notation in [7] for the foundations of the theory, where ω only denotes orientation, one can make the theory applicable to both the rigid and flexible cases.)

Note that the general formulae in this section are for systems with molecular solvent. In the primitive model the Coulomb potential is $\phi_{\text{Coul}}/\epsilon_r$ rather than ϕ_{Coul} . When we apply the general formulae in this model we will therefore have to insert factors of ϵ_r in appropriate places.

3.1. Yukawa function decay of the screened Coulomb potential

For the systems considered here the unit screened Coulomb potential, as defined in section 2, decays for large r like [7]

$$\phi_{\text{Coul}}^0(r) \sim \frac{e^{-\kappa r} \phi_{\text{Coul}}(r)}{E_r} = \frac{e^{-\kappa r}}{4\pi E_r \epsilon_0 r}, \quad (15)$$

where E_r is an effective relative permittivity of the electrolyte solution ($E_r \epsilon_0$ is an effective permittivity). This asymptotic result holds provided the electrolyte concentration is not too high (the range of validity depends on the system). In the limit of infinite dilution of the electrolyte we have

$$\phi_{\text{Coul}}^0(r) \sim \frac{e^{-\kappa_D r} \phi_{\text{Coul}}(r)}{\epsilon_r} = \frac{e^{-\kappa_D r}}{4\pi \epsilon_r \epsilon_0 r} \quad (\text{infinite dilution}) \quad (16)$$

when $r \rightarrow \infty$, where κ_D is the Debye screening parameter and κ_D^{-1} is the Debye length defined from

$$\kappa_D^2 = \frac{\beta}{\epsilon_r \epsilon_0} \sum_j n_j q_j^2 \quad (17)$$

where ϵ_r is the dielectric constant of the pure solvent, $\beta = (k_B T)^{-1}$, k_B is Boltzmann's constant, T is the absolute temperature and n_j is the number density of species j in the electrolyte solution. In equation (15) we have $\kappa \neq \kappa_D$ and $E_r \neq \epsilon_r$, but from the infinite dilution result it follows that $\kappa/\kappa_D \rightarrow 1$ and $E_r/\epsilon_r \rightarrow 1$ when the electrolyte concentration goes to zero. In pure solvent (where $\kappa = \kappa_D = 0$) equations (15) and (16) become equal to equation (13).

Let us first consider a solution of simple electrolytes, i.e. where the ions are small and spherical. In the PB approximation, which is a based on the primitive model but where the ion-ion correlations in the ion cloud around each ion are ignored (a mean field approximation), we have

$$\phi_{\text{Coul}}^0(r) = \frac{e^{-\kappa_D r} \phi_{\text{Coul}}(r)}{\epsilon_r} = \frac{e^{-\kappa_D r}}{4\pi \epsilon_r \epsilon_0 r} \quad (\text{PB}) \quad (18)$$

for all r and for any electrolyte concentration (both in the nonlinear and the linearized PB approximations). This is to be compared with the exact result (16) at infinite dilution, which is valid in the presence of molecular solvent but only asymptotically for large r . One should also compare with equation (15). While equation (18) is valid only in the PB approximation, equation (15) is an exact result both for the primitive model and for an electrolyte with molecular solvent.

In the PB approximation the dielectric function, equation (5), is given by

$$\frac{\tilde{\epsilon}(k)}{\epsilon_r} = 1 + \beta \sum_j n_j q_j^2 \frac{\tilde{\phi}_{\text{Coul}}(k)}{\epsilon_r} = \frac{k^2 + \kappa_D^2}{k^2} \quad (\text{PB}). \quad (19)$$

Here $\tilde{\epsilon}(k)/\epsilon_r$ is the dielectric function relative to a dielectric continuum with dielectric constant ϵ_r (as used in the primitive model) and $\tilde{\epsilon}(k)$ is the usual one (in vacuum).

For completeness we mention that the results (15), (16) and (18) can be inferred mathematically from the fact that a Yukawa function $\exp(-\kappa r)/r$ decay of a function $f(r)$ when $r \rightarrow \infty$ corresponds to a simple pole of $\tilde{f}(k)$ in complex k space at $k = i\kappa$, where i is the imaginary unit. (See [24] for a lucid description of the relationship between the long-range asymptotic behaviour and singularities in k space.) From equation (7) we see that $\tilde{\phi}_{\text{Coul}}^0(k)$ has a pole when $\tilde{\epsilon}(k) = 0$ and hence the $\exp(-\kappa r)/r$ decay corresponds to $\tilde{\epsilon}(i\kappa) = 0$. (The zero of the rhs of equation (19) at $k = i\kappa_D$ is obvious.) In general, the singularity of $\tilde{\phi}_{\text{Coul}}^0(k)$ in complex k space that lies closest to the real axis (the 'leading singularity') determines the leading asymptotic term of $\phi_{\text{Coul}}^0(r)$ when $r \rightarrow \infty$. Thus, when the pole at $k = i\kappa$ is the leading singularity, $\phi_{\text{Coul}}^0(r)$ decays like $\exp(-\kappa r)/r$. From these facts one can show that the factor E_r in the denominator of equation (15) is given by

$$E_r = \left[\frac{k}{2} \frac{d\tilde{\epsilon}(k)}{dk} \right]_{k=i\kappa} \quad (20)$$

which follows from residue calculus.

For a solution of a simple electrolyte with molecular solvent, the decay parameter κ is given by the expression [7]

$$\kappa^2 = \frac{\beta}{\epsilon_0} \left[\sum_{j \in \text{ions}} n_j q_j q_j^0 + n_s \langle \tilde{\sigma}_s \tilde{\rho}_s^0 \rangle_\omega \right]_{k=i\kappa} \quad (21)$$

where the sum is over the ionic species (cf equation (17)) and q_j^0 is the effective charge of a j ion (cf equation (9)). In the second term, which contains the solvent contributions (index $s = \text{solvent}$), n_s is the number density of solvent molecules, $\tilde{\sigma}_s$ is the Fourier transform of the internal charge density of a solvent molecule, $\tilde{\rho}_s^0$ is the Fourier transform of the renormalized charge density (to be defined later, equations (27) and (28)) of the same solvent molecule, the underline means the complex conjugate and $\langle \cdot \rangle_\omega$ denotes the average over all orientations of the molecule (and, when appropriate, all conformations weighted according to their probability). Note that the rhs of equation (21) depends on κ , so the expression is an equation for κ that, in fact, is equivalent to $\tilde{\epsilon}(i\kappa) = 0$. The contribution from the solvent molecules in this equation transcends the solvent dielectric properties;

ρ_s^0 contains contributions from the ions around each solvent molecule and q_j^0 contains contributions from the solvent.

One can write equation (21) in a different, but equivalent, manner that is more similar to its limiting form at infinite dilution, equation (17). By separating out a part of the dielectric function that only involves solvent molecules, $\tilde{\epsilon}^{\text{polar}}(k)$, one can show that [7]

$$\kappa^2 = \frac{\beta}{\tilde{\epsilon}^{\text{polar}}(ik)\epsilon_0} \left[\sum_{j \in \text{ions}} n_j q_j q_j^0 + n_s \left\langle \tilde{\sigma}_s \tilde{\rho}_s^{0,\text{ions}} \right\rangle_\omega \right]_{k=ik}, \quad (22)$$

where $\rho_s^{0,\text{ions}}$ is the part of the renormalized charge density of a solvent molecule that originates from the ions (for definitions of $\tilde{\epsilon}^{\text{polar}}$ and $\rho_s^{0,\text{ions}}$ and other details see [7]). In the limit of infinite dilution, $\tilde{\epsilon}^{\text{polar}}(k) \rightarrow \tilde{\epsilon}(k)$ for the pure solvent, and since $\kappa \rightarrow 0$ it follows that $\tilde{\epsilon}^{\text{polar}}(ik) \rightarrow \epsilon_r$, the dielectric constant for the solvent. Furthermore, $q_j^0 \rightarrow q_j$ and $\rho_s^{0,\text{ions}} \rightarrow 0$ in this limit, so equation (22) yields equation (17). Note that at *finite* electrolyte concentrations $\tilde{\epsilon}^{\text{polar}}$ is evaluated at $k = ik$ and not at $k = 0$. Physically this means that one considers the dielectric response due to an exponentially decaying electrostatic field rather than a uniform one.

In the primitive model the expression corresponding to equations (21) and (22) is [6]

$$\kappa^2 = \frac{\beta}{\epsilon_r \epsilon_0} \sum_{j \in \text{ions}} n_j q_j q_j^0. \quad (23)$$

The similarity to the definition of κ_D in equation (17) is obvious, and since the effective ionic charge q_j^0 is different from the bare charge q_j it is readily seen that $\kappa \neq \kappa_D$, as inferred above.

As we have seen in equation (9), the total potential from a simple ion in an electrolyte solution is proportional to the unit screened Coulomb potential $\phi_{\text{Coul}}^0(r)$ with the effective charge q_j^0 as the prefactor with $q_j^0 \neq q_i$. This holds in the PB approximation as well as in the exact analysis. The reason that the decay parameter in the PB approximation is given by equation (17) rather than equation (23) is that the ions that surround the central ion are treated like point ions that do not correlate with each other. Only the central ion (of species i) has an effective charge that is different from its bare charge, while for all other ions $q_j^0 = q_j$ in the PB approximation. The latter ions determine the screening. Thus it is the different treatment of the other ions compared to the central ion that makes $\kappa = \kappa_D$ in the PB approximation.

The deviation of q_i^0 from q_i for the central ion is a consequence of the facts that it attracts counterions and repels coions and that all ions are excluded from its interior. In the linearized PB approximation (the Debye–Hückel theory) it is only the exclusion effect that gives rise to this deviation and we have $q_i^0 = q_i \exp(\kappa_D a)/(1 + \kappa_D a)$, where a is the radius of the excluded volume around the central ion. In the nonlinear PB approximation all of these effects contribute and q_i^0 depends in a quite complex nonlinear fashion on q_i . In the exact case the dependence of q_i^0 on q_i and other system parameters are even more complex since the value of q_i^0 is influenced by the many-body correlations that are neglected in the PB approximation.

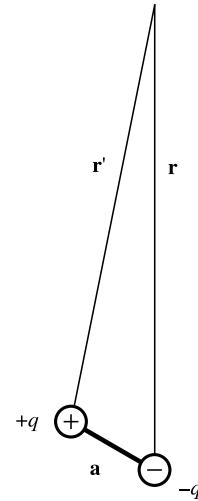


Figure 1. A dipole consisting of two charges $+q$ and $-q$ separated by the vector \mathbf{a} . Its dipole moment is $\mu = q\mathbf{a}$. The electrostatic potential is calculated at a point that lies at distances r' and r , respectively, from the charges.

Since all ions are then treated in the same manner, all ions of the same species have the same effective charge and $\kappa \neq \kappa_D$.

As we are now going to see, in the presence of molecular solvent it is not only the ions that give contributions to the effective charge, but also the solvent molecules. This may seem strange, since the solvent molecules are electroneutral and cannot give any contribution to a net charge. However, it is not the Coulombic charge of the molecules that matters in electrolytes, but rather a different entity that we will call the ‘Yukawa charge’ of the molecule.

3.2. How can an electroneutral molecule contribute to a net effective charge?

What does it mean that an electroneutral molecule gives a contribution to the effective charge of a particle in an electrolyte solution? We shall see that electrostatic potential from an ion and from a polar molecule in the cloud around the particle decays with distance in exactly the same way. Therefore, both contribute to the leading term in the potential far from the particle and thereby affect the value of the effective charge.

To see this, consider the potential from a dipole with the dipole moment $\mu = q\mathbf{a}$ as depicted in figure 1. In pure solvent ($\kappa = 0$) the Coulomb potential at a point located at the distance r' from the positive charge ($+q$) and distance r from the negative ($-q$) is proportional to

$$\frac{q}{r'} - \frac{q}{r} \sim \frac{q\mathbf{a} \cdot \hat{\mathbf{r}}}{r^2} = \frac{\mu \cdot \hat{\mathbf{r}}}{r^2} \quad \text{when } r \rightarrow \infty,$$

which is the normal dipolar term ($\hat{\mathbf{r}} = \mathbf{r}/r$ is the unit vector in the direction of \mathbf{r}). The potential decays faster than that from a charge since the inverse distance contributions from the two charges cancel exactly for large r .

In electrolytes ($\kappa \neq 0$), where the potential from a point charge decays like a Yukawa function, the potential from the

dipole is proportional to

$$\frac{qe^{-\kappa r'}}{r'} - \frac{qe^{-\kappa r}}{r} \sim \frac{qe^{-\kappa r}}{r} \left[e^{\kappa \mathbf{a} \cdot \hat{\mathbf{r}}} - 1 \right] \quad \text{when } r \rightarrow \infty.$$

The two Yukawa function contributions do *not* cancel and they give a contribution that decays *equally fast* as the potential from a charge, i.e. proportionally to $\exp(-\kappa r)/r$. The rhs depends on the direction of $\hat{\mathbf{r}}$, but there is a direction independent part which can be found by taking the average over all directions of $\hat{\mathbf{r}}$. The average of $\exp(\kappa \mathbf{a} \cdot \hat{\mathbf{r}})$ is equal to $\sinh(\kappa a)/(\kappa a)$, so the dipole gives the same contribution to the potential as a point charge $q[\sinh(\kappa a)/(\kappa a) - 1]$.

Thus it is not the Coulombic charge of a molecule that matters but a different entity, which we shall call the Yukawa charge of the molecule. The dipole in figure 1 has the ‘bare Yukawa charge’

$$q^* = q \left[\frac{\sinh(\kappa a)}{\kappa a} - 1 \right]. \quad (24)$$

This dipole also gives contributions to the potential with the same direction dependence as an ordinary dipole potential. One can show that

$$\frac{qe^{-\kappa r'}}{r'} - \frac{qe^{-\kappa r}}{r} \sim [q^* + \kappa \boldsymbol{\mu}^* \cdot \hat{\mathbf{r}} + \dots] \frac{e^{-\kappa r}}{r} + [\boldsymbol{\mu}^* \cdot \hat{\mathbf{r}} + \dots] \frac{e^{-\kappa r}}{r^2} + \dots \quad \text{when } r \rightarrow \infty, \quad (25)$$

where the bare ‘Yukawa dipole moment’ is

$$\boldsymbol{\mu}^* = \boldsymbol{\mu} \left[\frac{3 \cosh(\kappa a)}{(\kappa a)^2} - \frac{3 \sinh(\kappa a)}{(\kappa a)^3} \right] \quad (26)$$

and where the expansion continues with quadrupolar and higher multipolar terms. These higher moments have similar hyperbolic factors as in equations (24) and (26). When $\kappa \rightarrow 0$ an ordinary multipole expansion of the potential is obtained, $q^* \rightarrow 0$ and $\boldsymbol{\mu}^* \rightarrow \boldsymbol{\mu}$ (note the factor κ in front of the first $\boldsymbol{\mu}^*$ in equation (25)).

A very important difference between equation (25) and the ordinary multipole expansion is that the leading term that decays like $\exp(-\kappa r)/r$ contains contributions from *all orders of multipole moments*. The second leading term $\exp(-\kappa r)/r^2$ starts with a dipolar term and continues with all higher order multipole moments. The next term $\exp(-\kappa r)/r^3$ (not shown) starts with a quadrupolar term etc. Thus the direction dependence of the potential continues out to the far field region, which is very different from the case in pure solvent and in vacuum, where in the general case the spherically symmetric $1/r$ term from the net charge is the only contribution that survives far away. For a dipole it is only the dipolar term that survives far away in these cases.

Another difference between equation (25) and the ordinary multipole expansion is the following. In the ordinary expansion the lowest order nonzero multipole is independent of where we put the origin, while all higher order multipoles depend on this choice. For the Yukawa potential multipoles, *all* moments depend on the choice of origin including the lowest order one. If we selected to put the origin in figure 1 at the

charge $+q$ instead of $-q$ the sign of q^* would be reversed, and if we put the origin at the midpoint between the charges we would have $q^* = 0$. Since the oriented solvent molecules in the cloud surrounding a particle are normally located at off-centre positions relative to the particle, they will contribute to the net effective charge of the particle counted from its centre. Of course, these matters are equally relevant for contributions from solute molecules that surround the particle.

3.3. Renormalized charge density of molecules

The total electrostatic potential from a particle in solution consists of the potential from the particle itself and from particles in its surroundings. We have seen that the potential from a charge propagates in space according to the unit screened Coulomb potential $\phi_{\text{Coul}}^0(r)$, at least in the weak field limit. Furthermore, we saw in the previous subsection that the application of the screened Coulomb potential has important implication for the qualitative behaviour of the potential from a particle in electrolytes. If we want to apply $\phi_{\text{Coul}}^0(r)$ for calculation of the *total* electrostatic potential due to a particle, how do we proceed? Since $\phi_{\text{Coul}}^0(r)$, which we have defined for all r , expresses the linear part of response due to charges (more specifically, the self-consistent response to the total potential), there must be some means to treat the nonlinear part of the response to the interactions with the particle. This is where charge renormalization of particles comes in. As we shall see, the renormalization tells us how to include particles from the ‘ion and solvent cloud’ around each particle without double-counting the contributions already taken care of by ϕ_{Coul}^0 .

Let us consider a particle of species i immersed in an electrolyte solution and placed fixed at the origin and with a fixed orientation (and conformation) symbolized by ω . It is surrounded by a charge density of its cloud equal to $\rho_i^{\text{ex}}(\mathbf{r}; \omega)$ and the total charge density $\rho_i(\mathbf{r}; \omega)$ is given by equation (11). The electrostatic potential $\psi_i(\mathbf{r}; \omega)$ due to the particle is given by a simple application of Coulomb’s law, equation (12). (If we consider a particle immersed in a primitive model electrolyte ϕ_{Coul} should be replaced by $\phi_{\text{Coul}}/\epsilon_r$.)

Our task is to express the potential $\psi_i(\mathbf{r}; \omega)$ in terms of the unit screened Coulomb potential, $\phi_{\text{Coul}}^0(r)$, rather than the unscreened one, $\phi_{\text{Coul}}(r)$. We want to keep the same simple form of the expression for ψ_i as Coulomb’s law. To achieve this, we cannot, of course, simply insert ϕ_{Coul}^0 instead of ϕ_{Coul} in equation (12). The charge density must also be changed in order to give the same potential ψ_i . We therefore set

$$\psi_i(\mathbf{r}_{12}; \omega) = \int d\mathbf{r}_3 \rho_i^0(\mathbf{r}_{13}; \omega) \phi_{\text{Coul}}^0(r_{32}) \quad (27)$$

where ρ_i^0 , the *renormalized charge density*, is unambiguously defined from this equation. Note that equation (27) yields $\psi_i(\mathbf{r}_{12}; \omega)$ for all \mathbf{r}_{12} values and that $\psi_i(\mathbf{r}_{12}; \omega)$ is exactly the same in equations (12) and (27). Remember that $\phi_{\text{Coul}}^0(r_{32})$ is defined for all r_{32} by equation (8) (or equivalently by equation (6) or (7)).

The relationship between ρ_i and ρ_i^0 can be written in Fourier space as

$$\tilde{\rho}_i^0(\mathbf{k}; \omega) = \tilde{\rho}_i(\mathbf{k}; \omega) \tilde{\epsilon}(k), \quad (28)$$

which follows from $\tilde{\psi}_i = \tilde{\rho}_i \tilde{\phi}_{\text{Coul}} = \tilde{\rho}_i \tilde{\epsilon} \tilde{\phi}_{\text{Coul}}/\tilde{\epsilon} = \tilde{\rho}_i^0 \tilde{\phi}_{\text{Coul}}^0$, where we have used that the integrals in equations (12) and (27) are convolutions. For the primitive model the relationship is $\tilde{\rho}_i^0 = \tilde{\rho}_i \tilde{\epsilon}/\epsilon_r$ instead of equation (28). (We should mention here that ρ_i^0 can be expressed entirely in terms of ρ_j and σ_j for all j because the dielectric function can be written in terms of $\tilde{\rho}_j$ and $\tilde{\sigma}_j$. This follows from equation (5) and the linear response theory relation $\tilde{\chi}(k) = -\beta \sum_j n_j \langle \tilde{\sigma}_j \tilde{\rho}_j \rangle_\omega$. Incidentally, $\tilde{\chi}^0$ can be expressed in terms of $\tilde{\rho}_j^0$ and $\tilde{\sigma}_j$ in exactly the same manner, which lies behind the expression (21).)

The charge density $\rho_i^0(\mathbf{r}; \omega)$ consists of the bare charge density $\sigma_i(\mathbf{r}; \omega)$ of the particle and an additional charge distribution, $\rho_i^{\text{dress}}(\mathbf{r}; \omega)$, which is built up by the various species in the surrounding electrolyte solution, and we have

$$\rho_i^0(\mathbf{r}; \omega) = \sigma_i(\mathbf{r}; \omega) + \rho_i^{\text{dress}}(\mathbf{r}; \omega). \quad (29)$$

It is a nontrivial fact [6, 7] that $\rho_i^0(\mathbf{r}; \omega)$ is a more short-ranged function than $\rho_i(\mathbf{r}; \omega)$ (provided, as before, that we avoid systems that are close to critical states and systems with very strong screening, i.e. very short screening lengths). We denote $\rho_i^{\text{dress}}(\mathbf{r}; \omega)$ as the ‘dress’ of the particle and it constitutes an unambiguously defined, short-range part of $\rho_i^{\text{ex}}(\mathbf{r}; \omega)$. The particle and its dress will be denoted as a ‘dressed particle’, which accordingly has the charge distribution $\rho_i^0(\mathbf{r}; \omega)$.

One can show that [6, 7]

$$\rho_i^{\text{ex}}(\mathbf{r}_{12}; \omega) = \rho_i^{\text{dress}}(\mathbf{r}_{12}; \omega) + \int d\mathbf{r}_3 \psi_i(\mathbf{r}_{13}; \omega) \chi^0(r_{32}) \quad (30)$$

where χ^0 is the same response function as in equation (3). The integral is the linear part of the polarization response to the total potential ψ_i from the central i particle. This term constitutes the part of ρ_i^{ex} that is not contained in ρ_i^{dress} . It follows that ρ_i^{dress} contains the charge density due to the *nonlinear part* of the polarization response. By adding σ_i to both sides of equation (30) we obtain the same relationship between ρ_i and ρ_i^0 , that is $\rho_i = \rho_i^0 + \int \psi_i \chi^0$.

In the PB approximation this relationship between ρ_i and ρ_i^0 becomes particularly simple and can be written $\rho_i^0(\mathbf{r}; \omega) = \rho_i(\mathbf{r}; \omega) + \epsilon_0 \epsilon_r \kappa_D^2 \psi_i(\mathbf{r}; \omega)$, where ψ_i and ρ_i in this case can be determined by solving the nonlinear PB equation. Since $\phi_{\text{Coul}}^0(r)$ is equal to a Yukawa function for all r in the PB approximation, equation (18), we have from equation (27)

$$\psi_i(\mathbf{r}_{12}; \omega) = \frac{1}{4\pi \epsilon_r \epsilon_0} \int d\mathbf{r}_3 \rho_i^0(\mathbf{r}_{13}; \omega) \frac{e^{-\kappa_D r_{32}}}{r_{32}} \quad (\text{PB}) \quad (31)$$

i.e. ψ_i written as a superposition of Yukawa function contributions for all \mathbf{r}_{12} values. As mentioned earlier, in the PB approximation the ions in the cloud around the central i particle are treated like point ions that do not correlate with each other, which is the reason for the simplicity of this case.

In the exact treatment all particles are treated on the same fundamental level. Then, ψ_i is equal to a superposition of Yukawa potential contributions for large \mathbf{r}_{12} values only, i.e.

$$\psi_i(\mathbf{r}_{12}; \omega) \sim \frac{1}{4\pi E_r \epsilon_0} \int d\mathbf{r}_3 \rho_i^0(\mathbf{r}_{13}; \omega) \frac{e^{-\kappa r_{32}}}{r_{32}} \quad (32)$$

when $r_{12} \rightarrow \infty$, cf equation (15). Here it is equation (27) that gives ψ_i for all \mathbf{r}_{12} values, but then one must use $\phi_{\text{Coul}}^0(r_{32})$ for all r_{32} , which is not a simple Yukawa function for small r_{32} .

3.4. The asymptotic expansion of the electrostatic potential

From equation (32) one can show [12] that the leading contribution to $\psi_i(\mathbf{r}; \omega)$ for large r is

$$\psi_i(\mathbf{r}; \omega) \sim a_i^{(1)}(\hat{\mathbf{r}}; \omega) \frac{e^{-\kappa r}}{4\pi E_r \epsilon_0} \quad (33)$$

where

$$a_i^{(1)}(\hat{\mathbf{r}}; \omega) = \int d\mathbf{s} \rho_i^0(\mathbf{s}; \omega) \exp(-\kappa \mathbf{s} \cdot \hat{\mathbf{r}}), \quad (34)$$

(a Laplace transform), which gives the coupling between the renormalized charge density and an exponentially varying potential field in the direction $\hat{\mathbf{r}}$. Furthermore,

$$a_i^{(1)}(\hat{\mathbf{r}}; \omega) = q_i^0 + \kappa \boldsymbol{\mu}_i^0(\omega) \cdot \hat{\mathbf{r}} + \frac{\kappa^2}{3} \boldsymbol{\Theta}_i^0(\omega) : \hat{\mathbf{r}} \hat{\mathbf{r}} + \dots \quad (35)$$

where ‘ $:$ ’ denotes double contraction and the effective Yukawa charge and dipole and quadrupole moments of the dressed particle are given by

$$q_i^0 = \int d\mathbf{s} \rho_i^0(\mathbf{s}; \omega) \frac{\sinh(\kappa s)}{\kappa s} \quad (36)$$

$$\boldsymbol{\mu}_i^0(\omega) = 3 \int d\mathbf{s} \rho_i^0(\mathbf{s}; \omega) \mathbf{s} \left[\frac{\cosh(\kappa s)}{\kappa^2 s^2} - \frac{\sinh(\kappa s)}{\kappa^3 s^3} \right] \quad (37)$$

$$\boldsymbol{\Theta}_i^0(\omega) = \frac{15}{2} \int d\mathbf{s} \rho_i^0(\mathbf{s}; \omega) (3\mathbf{s}\mathbf{s} - s^2 \mathbf{1}) \times \left[\frac{\sinh(\kappa s)}{\kappa^3 s^3} - 3 \frac{\cosh(\kappa s)}{\kappa^4 s^4} + 3 \frac{\sinh(\kappa s)}{\kappa^5 s^5} \right]. \quad (38)$$

The next term in $\psi_i(\mathbf{r}; \omega)$ decays like $\exp(-\kappa r)/r^2$ and we have

$$\psi_i(\mathbf{r}; \omega) \sim \frac{e^{-\kappa r}}{4\pi E_r \epsilon_0} \left[\frac{a_i^{(1)}(\hat{\mathbf{r}}; \omega)}{r} + \frac{a_i^{(2)}(\hat{\mathbf{r}}; \omega)}{r^2} + \dots \right] \quad \text{when } r \rightarrow \infty, \quad (39)$$

where

$$a_i^{(2)}(\hat{\mathbf{r}}; \omega) = \boldsymbol{\mu}_i^0(\omega) \cdot \hat{\mathbf{r}} + \kappa \boldsymbol{\Theta}_i^0(\omega) : \hat{\mathbf{r}} \hat{\mathbf{r}} + \dots \quad (40)$$

The analogy to the case of a single dipole, equation (25), is obvious, and we see that the definitions (24) and (26) are special cases of equations (36) and (37). In equation (39) the subsequent term, which decays like $\exp(-\kappa r)/r^3$, starts with the quadrupolar term in the expansion of $a_i^{(3)}(\hat{\mathbf{r}}; \omega)$. The coefficients $a_i^{(l)}(\hat{\mathbf{r}}; \omega)$ for all l can also be expressed as integrals of ρ_i^0 [12].

When $\kappa \rightarrow 0$ (vanishing electrolyte concentration) only the charge term in $a_i^{(1)}(\hat{\mathbf{r}}; \omega)$ and the dipolar term in $a_i^{(2)}(\hat{\mathbf{r}}; \omega)$ survive and give the corresponding terms in the Coulombic multipole expansion (the same applies for the higher order terms not shown). In this limit $q_i^0 \rightarrow \int d\mathbf{s} \rho_i^0(\mathbf{s}; \omega) = \int d\mathbf{s} \sigma_i(\mathbf{s}; \omega) = q_i$ since electroneutral molecules in the dress do not give any contribution to the integral of ρ_i^0 . On the other hand, we have $\boldsymbol{\mu}_i^0(\omega) \rightarrow \int d\mathbf{s} \mathbf{s} \rho_i^0(\mathbf{s}; \omega)$, which is not equal to $\boldsymbol{\mu}_i(\omega) = \int d\mathbf{s} \mathbf{s} \sigma_i(\mathbf{s}; \omega)$, since we in general obtain a contribution from the dipolar moment of the dress. The higher order moments behave analogously.

In electrolyte solutions, $\kappa \neq 0$, the leading term (33) of the electrostatic potential at long distances contains contributions from **all** multipole moments, equation (35). Hence the effects of anisotropy of the central particle and its surrounding charge distribution survive far away from the molecule. This is radically different from the situation in pure solvent and in vacuum, where only the contribution from the highest nonzero multipole survives, e.g. the leading term for large r from an anisotropic charged particle is the isotropic r^{-1} contribution, while the dipolar contributions decay faster and the multipolar still faster.

Furthermore, the effective Yukawa charge and multipole moments of a particle in an electrolyte contain contributions from all kinds of charged and/or polar molecules in its dress. This includes contributions from electroneutral polar particles to the effective Yukawa charge as a special case. When the screening length κ^{-1} is large compared to the molecular size the contributions from electroneutral particles are small, but since there are many solvent molecules around a particle the contributions add up to a non-negligible number when κ^{-1} approaches the molecular size. Furthermore, polar solute molecules, when present, also contribute in the same manner.

3.5. The interaction free energy between two molecules in electrolytes

The renormalized charge density ρ_i^0 also has a fundamental role in the interaction between two particles of species i and j in an electrolyte solution. The appropriate entity here is the pair potential of mean force w_{ij} between the molecules or, in other words, the interaction free energy. The pair distribution function is given by $g_{ij} = \exp(-\beta w_{ij})$. As shown in [7], the screened electrostatic part of the potential of mean force, w_{ij}^{el} , can be written as the interaction between the renormalized charge distributions ρ_i^0 and ρ_j^0 of the molecules as mediated by the unit screened Coulomb potential

$$w_{ij}^{\text{el}}(\mathbf{r}_{12}; \omega_1, \omega_2) = \int d\mathbf{r}_3 d\mathbf{r}_4 \rho_i^0(\mathbf{r}_{13}; \omega_1) \phi_{\text{Coul}}^0(r_{34}) \rho_j^0(\mathbf{r}_{24}; \omega_2), \quad (41)$$

where the centres of the two molecules are separated by \mathbf{r}_{12} and they have orientations (and conformations) specified by ω_1 and ω_2 . This expression has the same formal appearance as an electrostatic interaction energy between two charge distributions expressed with Coulomb's law. It can alternatively be written

$$w_{ij}^{\text{el}}(\mathbf{r}_{12}; \omega_1, \omega_2) = \int d\mathbf{r}_4 \psi_i(\mathbf{r}_{14}; \omega_1) \rho_j^0(\mathbf{r}_{24}; \omega_2) \\ = \int d\mathbf{r}_3 \rho_i^0(\mathbf{r}_{13}; \omega_1) \psi_j(\mathbf{r}_{23}; \omega_2), \quad (42)$$

which has the form of an interaction energy expressed in terms of the electrostatic potential from one molecule and the renormalized charge density of the other. The interaction free energy w_{ij}^{el} is a distinct contribution to the complete w_{ij} , which can be written for all \mathbf{r}_{12} as [7]

$$w_{ij}(\mathbf{r}_{12}; \omega_1, \omega_2) = u_{ij}^{\text{short}}(\mathbf{r}_{12}; \omega_1, \omega_2) + w_{ij}^0(\mathbf{r}_{12}; \omega_1, \omega_2) \\ + w_{ij}^{\text{el}}(\mathbf{r}_{12}; \omega_1, \omega_2), \quad (43)$$

where u_{ij}^{short} is the short-range nonelectrostatic part of the pair potential between the i and j molecules and w_{ij}^0 contains the pair bridge function and a term that only involves the short-range correlation functions for the dresses of the molecules.

If the electrolyte concentration is not too high and the screening length therefore not too short, w_{ij}^{el} decays more slowly with distance than w_{ij}^0 and u_{ij}^{short} [6, 7]. The former contribution then dominates for large separations and we have $w_{ij}(\mathbf{r}_{12}; \omega_1, \omega_2) \sim w_{ij}^{\text{el}}(\mathbf{r}_{12}; \omega_1, \omega_2)$ when $r_{12} \rightarrow \infty$. The leading term of w_{ij} for large r_{12} then is

$$w_{ij}(\mathbf{r}_{12}; \omega_1, \omega_2) \sim \frac{1}{4\pi E_r \epsilon_0} \int d\mathbf{r}_3 d\mathbf{r}_4 \rho_i^0(\mathbf{r}_{13}; \omega_1) \\ \times \frac{e^{-\kappa r_{34}}}{r_{34}} \rho_j^0(\mathbf{r}_{24}; \omega_2), \quad (44)$$

where we have inserted the leading Yukawa function term of $\phi_{\text{Coul}}^0(r_{34})$ in w_{ij}^{el} . While this equation is valid for large r_{12} only, equation (43) with w_{ij}^{el} from equation (41) is valid for all \mathbf{r}_{12} .

Note that equations (41)–(43) bring an illustrative perspective on the assumptions in the PB approximation. In this approximation one sets $w_{ij}^{\text{el}} = \psi_i q_j$ and $w_{ij} = u_{ij}^{\text{short}} + w_{ij}^{\text{el}}$. Thereby, one has made two approximations: (i) that w_{ij}^{el} constitute the entire w_{ij} apart from u_{ij}^{short} and (ii) that ρ_j^0 is replaced by a point charge q_j in the first equality of equation (42) or, equivalently, in equation (41). Thus, only the i particle has a dress (the central particle), while all other particles are assumed to be undressed point ions. As a consequence $w_{ij} \neq w_{ji}$ in general, while in the correct theory we have $w_{ij} = w_{ji}$ as required. We have already seen several other consequences of this approximation.

The potential of mean force can in the general case also be expressed in terms of the Yukawa charge and multipole moments. When the screening length is not too short the leading contribution decays for large separation like [7]

$$w_{ij}(\mathbf{r}; \omega_1, \omega_2) \sim a_i^{(1)}(\hat{\mathbf{r}}; \omega_1) a_j^{(1)}(-\hat{\mathbf{r}}; \omega_2) \frac{e^{-\kappa r}}{4\pi \epsilon_0 E_r r} \\ = \left[q_i^0 + \kappa \boldsymbol{\mu}_i^0 \cdot \hat{\mathbf{r}} + \frac{\kappa^2}{3} \boldsymbol{\Theta}_i^0 : \hat{\mathbf{r}} \hat{\mathbf{r}} + \dots \right] \\ \times \left[q_j^0 - \kappa \boldsymbol{\mu}_j^0 \cdot \hat{\mathbf{r}} + \frac{\kappa^2}{3} \boldsymbol{\Theta}_j^0 : \hat{\mathbf{r}} \hat{\mathbf{r}} + \dots \right] \\ \times \frac{e^{-\kappa r}}{4\pi E_r \epsilon_0 r}, \quad (45)$$

where \mathbf{r} points from the i molecule to the j molecule (for clarity ω_1 and ω_2 are suppressed in the moments). For two spherically symmetric particles this becomes

$$w_{ij}(r) \sim \frac{q_i^0 q_j^0 e^{-\kappa r}}{4\pi \epsilon_0 E_r r} \quad (46)$$

for large r . We have $w_{ij}(r) \sim q_i^0 \psi_j(r) \sim q_i^0 \psi_j(r)$ in this case, i.e. the interaction free energy between the particles decays like the mean potential from one particle times the Yukawa charge of the other. The asymptotic relationships (45) and (46) constitute the exact results that correspond to the weak overlap approximation for the double layers of two interacting particles in electrolytes.

Note that if species i and j are at infinite dilution, e.g. single particles immersed in an electrolyte solution with a finite salt concentration, $a_i^{(l)}(\hat{\mathbf{r}}; \omega)$ for species i can be evaluated in the absence of species j and vice versa. Their interaction when both are present (at infinite dilution) satisfies equation (45) with a Yukawa function decay where κ and E_r have the values of the pure bulk electrolyte solution.

3.6. Higher order terms

We have so far considered the leading term of $\phi_{\text{Coul}}^0(r)$, which decays like $\exp(-\kappa r)/r$ for the systems studied here. We shall briefly consider higher order terms that decay faster. They give contributions to ψ_i and w_{ij} that are included in equations (27) and (41), but of course not in equations (32) and (44).

Such a contribution can be another Yukawa function term that decays like $\exp(-\kappa' r)/r$ with $\kappa' > \kappa$. This is of special interest for instance for 1:2 electrolytes where the decay lengths κ^{-1} and $(\kappa')^{-1}$ have similar magnitudes in a fairly wide concentration interval [25, 26], and we have for large r

$$\phi_{\text{Coul}}^0(r) \sim \frac{e^{-\kappa r}}{4\pi E_r \epsilon_0 r} + \frac{e^{-\kappa' r}}{4\pi E'_r \epsilon_0 r}, \quad (47)$$

where E'_r is a constant analogous to E_r , see below. The second term gives contributions to ψ_i and w_{ij} analogous to the rhs of equations (32) and (44). These contributions can also be expanded asymptotically for large r as the rhs of equations (39) and (45), but $a_i^{(l)}(\hat{\mathbf{r}}; \omega)$ and the Yukawa charge and multipole moments should be evaluated with κ replaced by κ' in the respective formulae above.

Both Yukawa function contributions in equation (47) correspond to zeros of $\tilde{\epsilon}(k)$ in the denominator of $\phi_{\text{Coul}}^0(k)$ in equation (7), i.e. $\tilde{\epsilon}(i\kappa) = 0$ and $\tilde{\epsilon}(i\kappa') = 0$. The factor E'_r in the second denominator of equation (47) is accordingly obtained from equation (20) by inserting $k = i\kappa'$ instead of $i\kappa$. An interesting fact is that $E_r > 0$ while $E'_r < 0$. When the electrolyte concentration is increased, κ and κ' approach each other and finally merge. For even higher concentrations $\phi_{\text{Coul}}^0(r)$ becomes an exponentially damped oscillatory function for large r , which correspond to a complex valued κ , see the appendix.

For completeness it should be mentioned that there exist terms in $\phi_{\text{Coul}}^0(r)$ with other r dependences. They correspond to singular points of $\tilde{\phi}_{\text{Coul}}^0(k)$ in complex k space that are not poles [6, 25]. Such a point is a singularity of $\tilde{\epsilon}(k)$ too and gives rise to a term in $\phi_{\text{Coul}}^0(r)$ that does not decay like a Yukawa function. If the singularity occurs at a point $i\zeta$ with real ζ , the decay in r space goes like $f(r) \exp(-\zeta r)$ with some different $f(r)$. (An example is a contribution that decays like the square of a Yukawa function, $\exp(-2\kappa r)/r^2$. This corresponds for spherically symmetric functions to a logarithmic branch point in complex k space at $k = i2\kappa$.) At least when the electrolyte concentration is sufficiently low, such singularities only give rise to higher order terms in $\phi_{\text{Coul}}^0(r)$.

3.7. An alternative charge density renormalization

As an alternative to equation (27) one can in the general case envisage a renormalized charge distribution $\rho_i^\otimes(\mathbf{r}; \omega)$ defined

such that

$$\psi_i(\mathbf{r}_{12}; \omega) = \frac{1}{4\pi \epsilon_0 E_r} \int d\mathbf{r}_3 \rho_i^\otimes(\mathbf{r}_{13}; \omega) \frac{e^{-\kappa r_{32}}}{r_{32}} \quad (48)$$

holds for all \mathbf{r}_{12} values with the correct $\psi_i(\mathbf{r}_{12}; \omega)$, κ and E_r . The screened Coulomb potential used would then be

$$\phi_{\text{Coul}}^\otimes(r) = \frac{e^{-\kappa r}}{4\pi E_r \epsilon_0 r} \quad (49)$$

for all r and we have

$$\psi_i(\mathbf{r}_{12}; \omega) = \int d\mathbf{r}_3 \rho_i^\otimes(\mathbf{r}_{13}; \omega) \phi_{\text{Coul}}^\otimes(r_{32}). \quad (50)$$

One can easily show that

$$\rho_i^\otimes(\mathbf{r}; \omega) = [\rho_i(\mathbf{r}; \omega) + \epsilon_0 \kappa^2 \psi_i(\mathbf{r}; \omega)] E_r \quad (51)$$

(for the primitive model we have instead $\rho_i^\otimes = [\rho_i + \epsilon_r \epsilon_0 \kappa^2 \psi_i] E_r / \epsilon_r$). Clearly, ρ_i^\otimes is much simpler to evaluate in practice than ρ_i^0 . This is in particular the case for a single particle (e.g. a macromolecule of species i) immersed in an electrolyte solution of known κ and E_r .

Let us analogously define

$$w_{ij}^\otimes(\mathbf{r}_{12}; \omega_1, \omega_2) = \int d\mathbf{r}_3 d\mathbf{r}_4 \rho_i^\otimes(\mathbf{r}_{13}; \omega_1) \phi_{\text{Coul}}^\otimes(r_{34}) \rho_j^\otimes(\mathbf{r}_{24}; \omega_2) \\ = \frac{1}{4\pi \epsilon_0 E_r} \int d\mathbf{r}_3 d\mathbf{r}_4 \rho_i^\otimes(\mathbf{r}_{13}; \omega_1) \frac{e^{-\kappa r_{34}}}{r_{34}} \rho_j^\otimes(\mathbf{r}_{24}; \omega_2) \quad (52)$$

cf equations (41) and (44). While ψ_i in equation (50) is the same as in equation (27), w_{ij}^\otimes is not the same as w_{ij}^{el} in equation (41). One can, however, show that $w_{ij}^{\text{el}}(\mathbf{r}_{12}; \omega_1, \omega_2) \sim w_{ij}^\otimes(\mathbf{r}_{12}; \omega_1, \omega_2)$ for large r (this follows from $\tilde{w}_{ij}^\otimes(\mathbf{k}; \omega_1, \omega_2) = \tilde{w}_{ij}^{\text{el}}(\mathbf{k}; \omega_1, \omega_2) \tilde{s}(k)$, where $\tilde{s}(k) = (1 + \kappa^2/k^2) E_r / \tilde{\epsilon}(k)$, and the fact that $\tilde{s}(k) \rightarrow 1$ when $k \rightarrow i\kappa$). Thus we obtain the leading term of w_{ij} correctly. This holds provided, as stated above, that the screening length is not too short.

An advantage with this charge distribution renormalization is that it yields the correct electrostatic potential *everywhere* by applying a simple Yukawa function, but a disadvantage is that it gives correctly *only* the leading terms with decay length κ^{-1} of the screened electrostatic part of the interaction free energy (the higher order terms with shorter decay lengths are severely distorted from an appearance of $[\tilde{\epsilon}(k)]^2$ in the denominator of \tilde{w}_{ij}^\otimes rather than a single factor $\tilde{\epsilon}(k)$). It is *only* the fundamental renormalization defined by equation (27) that gives all terms correctly.

If one is interested only in the leading term in w_{ij} with decay length κ^{-1} one can calculate $a_i^{(1)}(\hat{\mathbf{r}}; \omega)$ in equation (34) by using the alternative renormalization given by equation (51). If one inserts ρ_i^\otimes instead of ρ_i^0 in equation (34) one obtains *exactly the same value* of $a_i^{(1)}(\hat{\mathbf{r}}; \omega)$ (this follows from $\tilde{\rho}_i^\otimes(\mathbf{k}; \omega) = \tilde{\rho}_i^0(\mathbf{k}; \omega) \tilde{s}(k)$ and the convolution theorem for the Fourier and Laplace transforms). This route is easier to apply and is particularly useful for the leading term of the interaction between two single particles (e.g. macromolecules of species i and j) immersed in an electrolyte solution of known κ and E_r .

4. Electrolytes with intermolecular dispersion interactions

4.1. Power law interactions

We shall now consider electrolytes that have contributions that decay like power laws, $r^{-\nu}$, in the nonelectrostatic part of their pair potential. The most important case is the ubiquitous dispersion interaction between molecules that decay for large r like r^{-6} . In liquid models it is usually included in the molecular interactions as a Lennard-Jones potential.

For systems of *uncharged* particles with pair interactions that decay like $r^{-\nu}$ with $\nu > 3$ it is known [27, 28] that their pair correlations $h(r)$ also decay like $r^{-\nu}$. More precisely, if the pair potential $u(r) \sim -\gamma r^{-\nu}$, where γ is a constant, then $h(r) \sim \beta K^2 \gamma r^{-\nu}$. The constant K is dimensionless and proportional to the isothermal compressibility χ_T

$$K = k_B T n \chi_T = k_B T \left(\frac{\partial n}{\partial P} \right)_{N,T} \quad (53)$$

where P is the pressure and N is the number of particles (we assume here as in the rest of the paper that we are not at criticality of the fluid).

This decay law for the correlation function *also holds for an electrolyte* [15]. If the nonelectrostatic interactions between the ions in a simple electrolyte decay like $-\gamma_{ij} r^{-\nu}$ for large r then $h_{ij}(r) \sim \beta K^2 \gamma_{NN} r^{-\nu}$, where γ_{NN} is a linear combination of γ_{ij} (to be defined below). This means that in the presence of power law interactions the ultimate decay of the pair correlations in an electrolyte is a power law rather than an exponential decay. When γ_{ij} and/or the compressibility is large, the $r^{-\nu}$ tail of $h_{ij}(r)$ is large. (In the primitive model of electrolyte solutions the number density we consider here is the ionic concentration and the pressure and compressibility refers to the ionic species only. We will for simplicity not treat solvent as a molecular species in this section and we will restrict ourselves to binary simple electrolytes. For a plasma consisting only of charged particles we consider, however, the total number density n , pressure and compressibility of the plasma.)

The presence of an $r^{-\nu}$ term in the pair interactions generates a multitude of power law contributions $r^{-\eta}$ with $\eta > \nu$ in the pair correlations; contributions that decay faster with r . Since the leading contribution $\beta K^2 \gamma_{NN} r^{-\nu}$ to the pair correlation function $h_{ij}(r)$ is equal for all species of ions it does not contribute to the charge density around the ions $\rho_i^{\text{ex}}(r) = \sum_j q_j n_j h_{ij}(r)$ since $\sum_j q_j n_j = 0$ from electroneutrality. Thus $\rho_i^{\text{ex}}(r)$ decays faster to zero when $r \rightarrow \infty$. To see how the charge density behaves it is very useful to introduce the ionic density-density, charge-charge and charge-density correlation functions $h_{NN}(r)$, $h_{QQ}(r)$ and $h_{QN}(r)$ (for a primitive model electrolyte solution they express the ionic concentration-concentration, charge-charge and charge-concentration correlations). In the density-density correlations one considers the spatial correlations in total number density of particles (irrespectively of species). Likewise, in the charge-charge and charge-density correlations all charges contribute in the same manner irrespectively of which species they belong

to; only the magnitude and sign of the charges matter. For a binary electrolyte we have

$$\begin{aligned} h_{NN} &= \theta_+^2 h_{++} + 2\theta_+ \theta_- h_{+-} + \theta_-^2 h_{--} \\ h_{QQ} &= \frac{1}{4} [h_{++} - 2h_{+-} + h_{--}] \end{aligned} \quad (54)$$

$$h_{QN} = h_{NQ} = \frac{1}{2} [\theta_+ h_{++} + (\theta_- - \theta_+) h_{+-} - \theta_- h_{--}]$$

where $\theta_i = n_i/n$ is the fraction of i ions and $n = n_+ + n_-$ is the total ionic number density. (This equation will also be used for γ_{ij} to define γ_{NN} , γ_{QN} and γ_{QQ} .) Conversely, we have

$$h_{ij} = h_{NN} + (t_i + t_j) h_{QN} + t_i t_j h_{QQ} \quad (55)$$

where $t_l = q_l/q_Q$ and $q_Q = (q_+ + |q_-|)/2$. We see from equation (55) that the species dependent contributions in $h_{ij}(r)$ come from the $h_{QN}(r)$ and $h_{QQ}(r)$ terms while the contribution from $h_{NN}(r)$ is the same for all species. The decay of $h_{ij}(r)$ we mentioned above originates from the fact that $h_{NN}(r) \sim \beta K^2 \gamma_{NN} r^{-\nu}$ in the presence of the power law interaction.

The charge density $\rho_i^{\text{ex}}(r)$ can be written as

$$\rho_i^{\text{ex}}(r) = nq \left(h_{QN}(r) + \frac{q_i}{q_Q} h_{QQ}(r) \right) \quad (56)$$

where $q = (n_+ q_+ + n_- |q_-|)/n$. Here we see that the contribution from the term with $h_{QQ}(r)$ depends on the sign of the ionic charge while that from $h_{QN}(r)$ is the same for anions and cations. Note that the relationships (54)–(56) hold for binary electrolytes irrespectively of the pair interactions.

In the present case with power law interactions, $h_{NN}(r)$, $h_{QN}(r)$ and $h_{QQ}(r)$ decay in general like $r^{-\nu}$, $r^{-(\nu+2)}$ and $r^{-(\nu+4)}$ respectively [15] when the nonelectrostatic part of the pair potential decays like $r^{-\nu}$ with $\nu > 3$. This implies that $\rho_i^{\text{ex}}(r)$ decays like $r^{-(\nu+2)}$, i.e. it too follows a power law rather than an exponential decay for large r . The part of the charge distribution that depends on sign of the ionic charge decays like $h_{QQ}(r)$, i.e. like $r^{-(\nu+4)}$.

The polarization response function $\chi(r)$ in equation (3) can explicitly be written in terms of the charge-charge correlations as

$$\chi(r) = -\beta nq [q_Q \delta^{(3)}(r) + nq h_{QQ}(r)], \quad (57)$$

which accordingly decays like $r^{-(\nu+4)}$ for large r . Consider the response due to a small point charge placed at the origin. It follows from equation (3) with Ψ^{Ext} proportional to $\phi_{\text{Coul}}(r)$ that the polarization charge density from a small point charge decays like $r^{-(\nu+2)}$ in the linear regime. The total potential from the point charge and the polarization charge density therefore decays like $r^{-\nu}$, which follows from an integration of the Poisson equation. Thus the unit screened Coulomb potential $\phi_{\text{Coul}}^0(r)$ from equation (8) decays like $r^{-\nu}$ when $r \rightarrow \infty$, i.e. the same power as in the nonelectrostatic part of the pair potential. All these results show that the presence of a power law potential in addition to the Coulomb potential gives very different qualitative behaviour for large r compared to the previous case without such interactions.

4.2. Dispersion interactions between ions

Let us now specialize to the case of dispersion interactions between the ions, $\gamma_{ij}r^{-\nu}$ with $\nu = 6$. Then the density-density correlations $h_{NN}(r)$ decay like r^{-6} , charge-density correlations $h_{QN}(r)$ like r^{-8} and charge-charge correlations $h_{QQ}(r)$ like r^{-10} . This behaviour is, in fact, fundamental for fluids of charged particles. In quantum statistical mechanics for Coulomb fluids, where the particles *only* interact with Coulombic r^{-1} interactions apart from a hard core potential, $h_{NN}(r)$, $h_{QQ}(r)$ and $h_{QN}(r)$ decay exactly in this manner [29, 30]. These power law decays are a consequence of the quantum fluctuations that also give rise to the dispersion interaction. Thus, in classical statistical mechanics the inclusion of a r^{-6} potential term as an effective dispersion interaction gives rise to the correct asymptotic behaviour of the pair correlation functions for long distances.

We shall now in more detail treat a model electrolyte with the pair interaction

$$u_{ij}(r) = q_i q_j \phi_{\text{Coul}}(r) - \frac{\gamma_{ij}}{r^6} + u_{ij}^{\text{short}}(r) \quad (58)$$

where u_{ij}^{short} is any sufficiently short-range interaction. It may, for example, include the repulsive r^{-12} part of a Lennard-Jones potential (which generates power law $r^{-\eta}$ contributions with $\eta \geq 12$ in the correlation functions) or be of finite range like a hard core potential. In the primitive model we replace ϕ_{Coul} by $\phi_{\text{Coul}}/\epsilon_r$. When the polarizability of an ion is smaller than that of the solvent we may have a negative γ_{ij} . For a plasma in vacuum all γ_{ij} are positive.

We have [15] when $r \rightarrow \infty$

$$\begin{aligned} h_{NN}(r) &\sim \frac{\Lambda_{NN}}{r^6} \\ h_{QN}(r) &\sim -30 \frac{\Lambda_{QN}}{r^8} \\ h_{QQ}(r) &\sim 1680 \frac{\Lambda_{QQ}}{r^{10}}, \end{aligned} \quad (59)$$

where Λ_{IJ} are state dependent constants

$$\begin{aligned} \Lambda_{NN} &= \beta K^2 \sum_{ij} \theta_i \theta_j \gamma_{ij} = \beta K^2 \gamma_{NN} \\ \Lambda_{QN} &= \frac{\beta K}{\kappa_D^2} \sum_{ij} b_i \theta_j \gamma_{ij} = \beta K \left[\frac{\gamma_{QN}}{\kappa_D^2} + B \gamma_{NN} \right] \\ \Lambda_{QQ} &= \frac{\beta}{\kappa_D^4} \sum_{ij} b_i b_j \gamma_{ij} = \beta \left[\frac{\gamma_{QQ}}{\kappa_D^4} + 2B \frac{\gamma_{QN}}{\kappa_D^2} + B^2 \gamma_{NN} \right], \end{aligned} \quad (60)$$

where $b_{\pm} = B \kappa_D^2 \theta_{\pm} \pm \frac{1}{2}$ and B is a state dependent constant that can be written in terms of the second moment of $h_{QN}(r)$

$$B = -\frac{n}{6} \int d\mathbf{r} r^2 h_{QN}(r) \quad (61)$$

(in the notation of [15] $B = K \tau n / \kappa_D^2$).

It is most significant that Λ_{QN} and Λ_{QQ} depend on the ratio of the strengths of the dispersion interactions (γ_{ij}) and the

electrostatic coupling (κ_D^2 or κ_D^4). Both Λ_{NN} and Λ_{QN} depend on the compressibility (via K). In the general case Λ_{NN} , Λ_{QN} and Λ_{QQ} can be positive or negative, but if all $\gamma_{ij} > 0$ we always have $\Lambda_{NN} > 0$. B can have either sign.

If the dispersion interaction satisfies the ‘mixing rule’ $\gamma_{ij} = (\gamma_{ii} \gamma_{jj})^{1/2}$ we have

$$\Lambda_{QQ} \Lambda_{NN} = (\Lambda_{QN})^2, \quad (62)$$

which motivates why the numerical factors for h_{QQ} and h_{NQ} in equation (59) are not included in Λ_{IJ} . In this case $\Lambda_{NN} > 0$ and $\Lambda_{QQ} \geq 0$, while Λ_{QN} can be positive or negative. The term γ_{QN} in Λ_{QN} and Λ_{QQ} is here proportional to $\sqrt{\gamma_{++}} - \sqrt{\gamma_{--}}$ so its sign depends on the relative strength of the dispersion interactions between anions and between cations.

4.3. The screened Coulomb potential

From our results for $r^{-\nu}$ interactions at the end of section 4.1 it follows that the screened Coulomb potential decays like r^{-6} when $\nu = 6$. More precisely, we have when $r \rightarrow \infty$

$$\phi_{\text{Coul}}^0(r) \sim -\frac{L_{QQ}}{r^6}, \quad (63)$$

where $L_{QQ} = \Lambda_{QQ} \kappa_D^4 / (\beta q_Q^2)$ which we can write

$$L_{QQ} = \sum_{ij} b_i b_j \frac{\gamma_{ij}}{q_Q^2} = \frac{1}{q_Q^2} [\gamma_{QQ} + 2B \kappa_D^2 \gamma_{QN} + B^2 \kappa_D^4 \gamma_{NN}]. \quad (64)$$

Thus the ratio between the strength of the dispersion pair interactions and the square of the average ionic charge q_Q enters the coefficient L_{QQ} . When $B \kappa_D^2$ is small $L_{QQ} \approx \gamma_{QQ} / q_Q^2 = (\gamma_{++} - 2\gamma_{+-} + \gamma_{--}) / (q_+ + |q_-|)^2$, which is entirely determined by the interaction potential parameters. Note that if the mixing rule for γ_{ij} is satisfied $\gamma_{QQ} = (\sqrt{\gamma_{++}} - \sqrt{\gamma_{--}})^2$.

The spatial propagation of the electrostatic potential like an r^{-6} power law is intimately linked with the polarization of the electrolyte brought about by unequal dispersion interactions between the various ions. A separation of charge in one region does not only give rise to an electrostatic potential that polarizes other regions, but also a change in the dispersion interaction between the regions that is unequal for the various ions and therefore leads to a further contribution to the polarization. The dispersion interactions are not screened by the ions and therefore remain relatively long ranged. The net polarization charge density decays, as we have seen above, like r^{-8} . The expression (64) for L_{QQ} gives the appropriate weighing of the dispersion and electrostatic effects in this polarization.

That $\phi_{\text{Coul}}^0(r)$ ultimately decays like r^{-6} for large r does not prevent it from having an exponential decay for smaller r . As we have seen above such a decay is connected to a zero of the dielectric function, $\tilde{\epsilon}(k) = 0$, in complex k space and a leading zero $k = ik$ still exists in the current case. The presence of a power law r^{-6} interaction in the pair potential prevents, however, a zero $k = ik$ with a real κ value from occurring [16]. Thus κ is complex valued here and, as discussed in the appendix, this leads to a term in $\phi_{\text{Coul}}^0(r)$ that decays in

an *exponentially damped oscillatory manner*, as in the rhs of equation (A.1). This term is, however, not the leading term here and is ultimately dominated for large r by the power law contributions to $\phi_{\text{Coul}}^0(r)$. (A power law term gives rise to a singularity at $k = 0$, e.g. r^{-6} gives a $|k|^3$ term that is nonanalytic at $k = 0$. This is the basis of the asymptotic analysis above, see [15, 16].)

Thus the electrostatic and dispersion interactions are coupled in an intricate manner. The dispersion interaction does not only cause a long-range r^{-6} tail of the electrostatic potential, but it also causes the exponentially screened part of the potential to turn oscillatory. (Note that the mechanism for these oscillations is entirely different from those that occur for strong electrostatic coupling mentioned in section 3.6 and the appendix.) The oscillations remain at infinite dilution, but one can show [16] that the screening length ξ^{-1} and the wavelength $\lambda = 2\pi\eta^{-1}$ of the exponential decay, where $\xi = \text{Re}(\kappa)$ and $\eta = \text{Im}(\kappa)$, have the following limiting law in the infinite dilution limit: $\xi^{-1} \propto n^{-1/2}$ (as in the usual case) and $\lambda \propto n^{-3}$ when $n \rightarrow 0$. This means that the wavelength λ is proportional to the screening length to the sixth power in this limit, which implies that the exponential contribution has decayed to a very small number long before one single oscillation has occurred. For dilute electrolytes the oscillatory contribution is accordingly indistinguishable from a plain exponential one, i.e. the oscillations have no noticeable effects. When the electrolyte concentration is increased this relationship between the screening length and the wavelength no longer holds. Then the oscillations may be important (how high the electrolyte concentration has to be before this happens is still an open question). However, for very weak dispersion forces the wavelength will be large and the oscillations can be ignored (λ goes to infinity when all γ_{ij} go to zero).

We accordingly have a situation where the screened electrostatic potential decays like r^{-6} for long distances and has an exponentially (albeit oscillatory) decaying part that is important for smaller distances. Both $h_{QN}(r)$ and $h_{QQ}(r)$ have exponentially decaying parts with the same decay length and wavelength as $\phi_{\text{Coul}}^0(r)$ despite the fact that, as we have seen, the power law decays of these functions are different. (This follows from the fact that in Fourier space $\tilde{\epsilon}(k)$ occur in the denominator of all these functions, which therefore have the ik pole in common.)

The charge distribution around an i ion, $\rho_i^{\text{ex}}(r)$, accordingly also has an exponentially decaying part with this decay length and wavelength in addition to the power law contributions that dominate for large r . From equations (56) and (59) it follows that when $r \rightarrow \infty$

$$\rho_i^{\text{ex}}(r) \sim -30 \frac{nq\Lambda_{QN}}{r^8} \quad (65)$$

irrespectively of the sign of the ionic charge. The part of the charge distribution that depends on this sign comes from the h_{QQ} term in equation (56) and decays as $1680q_iq_Q^{-1}nq\Lambda_{QQ}r^{-10}$ (there are also contributions from $h_{QN}(r)$ that decay like r^{-10}). Since Λ_{QN} contains the compressibility via K in equation (60), the magnitude of the

r^{-8} tail of $\rho_i^{\text{ex}}(r)$ will be large when the compressibility is large (e.g. near a phase separation).

From equation (65) and Poisson's equation it follows that the electrostatic potential from an i ion decays like

$$\psi_i(r) \sim \frac{nq\Lambda_{QN}}{\epsilon_r\epsilon_0 r^6} \quad (66)$$

when $r \rightarrow \infty$, where we have included the factor ϵ_r in the denominator as applicable in the primitive model. The effective charge as defined in equation (9) is accordingly

$$q^0 = -\frac{q_Q\Lambda_{QN}}{\Lambda_{QQ}\kappa_D^2} \quad (67)$$

and is the same for both species. When the mixing rule for γ_{ij} is satisfied, the sign of q^0 is determined by Λ_{QN} . That q^0 has the same sign for anions and cations is a consequence of the fact that the h_{QN} term in (56) is the same for both species. The part of $\psi_i(r)$ that is species dependent decays like r^{-8} (it originates from the h_{QQ} term).

The occurrence of the fairly long-ranged charge distribution around the ion complicates charge density renormalization schemes like that in section 3.3. The screened Coulomb interaction does not account for all effects in the long-range part since the dispersion interactions in themselves give rise to polarization charges far away. Therefore it does not make the same physical sense to do a renormalization solely based on ϕ_{Coul}^0 as in equation (27), even if it is formally possible to do it in the same manner here. (If one does, one obtains a renormalized charge density that decays like r^{-6} , which is more long-ranged than the actual charge density.) The exponentially decaying parts of the charge density and electrostatic potential are, however, dominated by electrostatic effects, at least when the dispersion interactions are not too strong. When this is fulfilled, the qualitative picture obtained in section 3 will hold for these parts (except the oscillations) even in the presence of dispersion interactions, but one cannot simply take over the formulae for the asymptotic relationships in section 3.4 as they stand since they do not properly consider the power law decays. The magnitude of the power law parts of ρ_i^{ex} and ψ_i can be obtained from the results in this section.

5. Summary

An exact statistical mechanical formalism for the screened electrostatic potential from and interaction between ions and molecules in electrolyte solutions with molecular solvent is presented. Key concepts are (i) the unit screened Coulomb potential $\phi_{\text{Coul}}^0(r)$, which gives the weak field propagation of the electrostatic potential (the Green's function of the electrolyte), and (ii) the renormalized charge density ρ_i^0 of each molecule. The latter contains the nonlinear polarization response of the electrolyte solution due to the interactions with the molecule. The average electrostatic potential ψ_i from a molecule is written, equation (27), in terms of ϕ_{Coul}^0 and ρ_i^0 in complete analogy to Coulomb's law. The screened electrostatic interaction free energy of two molecules, w_{ij}^{el} , in the solution is similarly expressed as the Coulomb-like

interaction between the renormalized charge density of one molecule, ρ_i^0 , and that of the other, ρ_j^0 , as mediated by the unit screened Coulomb potential ϕ_{Coul}^0 (equation (41)). These expressions for ψ_i and w_{ij}^{el} are valid for all distances. The long distance asymptotic decay behaviours of these functions are investigated and it is shown how they can be expressed in terms of multipole expansions based on the Yukawa function family $\exp(-\kappa r)/r^m$. The effective net charge, effective dipole moment and higher multipole moments of each molecule in the system are thereby defined. The expressions for these quantities (the Yukawa charge, Yukawa dipole moment etc) differ from the ordinary Coulombic ones. In an electrolyte solution all multipole moments contribute to the leading asymptotic term for large separations, which implies that the full directional dependence of the electrostatic potential from a molecule remains in the longest range tail. These decay behaviours are strictly valid provided the nonelectrostatic part of the molecular pair interactions decays faster than any power law and provided the electrolyte concentration is not too high (the screening length κ^{-1} not too short) and the system is not close to criticality.

In the presence of dispersion interactions between the particles in the electrolyte solution the exponential decay is no longer dominant in the electrostatics for large separations. Due to a nontrivial coupling between the electrostatic and dispersion pair interactions between the ions, the electrostatic potential from an ion ultimately decays like a power law for long distances. Furthermore, this coupling makes the exponentially decaying terms become oscillatory.

The main results for the long distance decay of the electrostatic potential for various cases are summarized in table 1.

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Appendix. Oscillatory screened Coulomb potential

The screened Coulomb potential $\phi_{\text{Coul}}^0(r)$ has in some cases an exponentially damped oscillatory decay or it can have a contribution with such behaviour. As we have seen, a nonoscillatory Yukawa function decay, equation (15), corresponds to a zero of the dielectric function $\tilde{\epsilon}(k)$ in complex k space (a pole of $\tilde{\phi}_{\text{Coul}}^0(k) = 1/[\epsilon_0 k^2 \tilde{\epsilon}(k)]$). We then have $\tilde{\epsilon}(ik) = 0$ with a real value κ , i.e. the zero ik occurs on the imaginary axis. Several such zeros can occur, e.g. ik' mentioned in section 3.6.

The dielectric functions can, however, also have a zero that does not lie on the imaginary axis. This corresponds to a solution of $\tilde{\epsilon}(i\zeta) = 0$ with a complex ζ . Such solutions always come in pairs, $\zeta = \xi + i\eta$ and its complex conjugate $\underline{\zeta} = \xi - i\eta$, where ξ and η are real. Together, these singularities of $\tilde{\phi}_{\text{Coul}}^0(k)$ give rise to a term in $\phi_{\text{Coul}}^0(r)$ that decays in an exponentially damped oscillatory manner, $\cos(\eta r + \vartheta) \exp(-\xi r)/r$, where

ϑ is a constant (a phase shift), cf [24]. In fact, the leading zero ik can be a solution of this kind and then we have for large r

$$\phi_{\text{Coul}}^0(r) \sim \cos(\eta r + \vartheta) \frac{e^{-\xi r}}{4\pi\epsilon_0\alpha r} \quad (\text{A.1})$$

where $\xi = \text{Re}(\kappa)$ and $\eta = \text{Im}(\kappa)$. The constants α and ϑ originate from E_r in equation (20), that is also complex valued here. Equation (A.1) holds as an asymptotic law provided no other, longer-ranged contributions exist. In the presence of nonelectrostatic power law interactions, section 4, such contributions do exist and then the rhs of equation (A.1) is a term in $\phi_{\text{Coul}}^0(r)$ that is dominated by the more long-ranged parts for large r .

A complex κ can, for example, arise when two purely imaginary zeros ik and ik' approach each other, then merge and finally give rise to two complex roots ik and $i\underline{\kappa}$. This happens in electrolyte solutions when the electrostatic coupling becomes strong enough, cf. section 3.6, a phenomenon that was first found by Kirkwood [31]. For sufficiently low electrolyte concentrations the leading singularity of $\tilde{\phi}_{\text{Coul}}^0(k)$ is, however, always a solution of $\tilde{\epsilon}(ik) = 0$ with a real κ for the systems treated in section 3.

For systems with dispersion interactions, section 4, κ is complex valued even at infinite dilution. This is caused by the appearance of a term proportional to k^3 in $\tilde{\epsilon}(k)$ from the r^{-6} interaction. This term together with other terms with higher odd powers of k prevent the zero at ik from appearing on the imaginary axis, at least when the electrolyte concentration is not too high [16].

The formulae in this paper can be generalized to accommodate complex κ and oscillatory Yukawa-like decays. This is left to future work.

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