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# Decay behavior of screened electrostatic surface forces in ionic liquids; the vital role of nonlocal electrostatics.

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Screened electrostatic surface forces, also called double layer forces, between surfaces in ionic liquids can, depending on circumstances, be decaying in an exponentially damped, oscillatory manner or in a plain exponential way (the latter like in dilute electrolyte solutions where ion-ion correlations are very weak). The occurrence of both of these behaviors in dense ionic liquids, where ion-ion correlations are very strong, is analyzed in the current work using exact statistical mechanics formulated in a manner that is physically transparent. A vital ingredient in an understanding of the decay behaviors is the fact that electrostatics in dense electrolytes have a nonlocal nature caused by the strong correlations. It is shown that effects of nonlocality can be elucidated by a remarkably simple, general expression for the decay parameter  $\kappa$  that replaces the classical expression for the inverse Debye length  $\kappa_{DH}$  of the Debye-Hückel (DH) and the nonlinear Poisson-Boltzmann approximations. This exact expression is valid for both the plain exponential and the oscillatory cases. It shows how strong correlations can give rise to plain exponential decay with a long decay length. Such a decay can arise from anion-cation associations of various kinds, for instance transient ion pairing or association caused by many-body correlations; ion pairing is a possibility but not a necessity for this to occur. The theoretical analysis is done for systems consisting of ions with arbitrary shape and internal charge density and immersed planar walls with arbitrary internal charge distribution and any short-ranged ion-surface interaction. The screened electrostatic surface force between two walls is at large separations proportional to the product of effective surface charge densities of each wall. For the oscillatory case, each wall contributes with a phase shift to the oscillations of the interaction.

### 1 Introduction

Ionic liquids are organic salts with melting points below 100  $^{\circ}$ C. Many are in the liquid state at room temperature. Several of their quite unique properties have given rise to a large interest for using them in various applications. They can, for example, be used as very stable solvents with extremely low vapor pressures and very special solvation attributes due to the ionic nature of the constituent molecules. Further examples include their use in supercapacitors, batteries and as lubricants. The reader is referred to Refs. 1–4 for reviews of properties of ionic liquids and several of their uses.

Measurements of surface interactions by the surface force apparatus or the atomic force microscope have shown that the measured force in ionic liquids in many cases is damped oscillatory. <sup>3,5–8</sup> Oscillations have been detected for surface separations

up to several nm. However, in some systems a long-ranged monotonic exponential decay has been observed with decay length 4-11 nm.  $^{9-11}$  The question whether these latter observations in any way can be attributed to diffuse double layer forces like in dilute electrolyte solutions has give rise to some controversy.  $^{12-14}$ These observations warrant a general theoretical analysis of electrostatic interactions in ionic liquids and other dense electrolytes. The fascinating properties of ionic liquids in general also motivate such an investigation.

It is well-known from classical statistical mechanics that the mean electrostatic potential from a particle in a simple electrolyte (i.e., electrolyte consisting of small spherical ions) is exponentially decaying at large distances either in a monotonic or an oscillatory manner. For a systematic molecular-dynamics simulation study of simple bulk electrolytes for various conditions from the plasma to the molten salt states, see Ref. 15. Consider a planar wall with a uniform surface charge density in contact with a bulk electrolyte. For such a system it is known that the mean electrostatic potential at distance z from the wall decays like  $exp(-\kappa z)$ 

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for large z in the case of monotonic decay, where  $\kappa$  is the decay parameter of the bulk electrolyte, and that it decays like an exponential times a cosine function in the oscillatory case. The latter behavior occurs, for instance, in molten simple salts and dense classical plasmas where the correlations between the ions are very strong, while the monotonic decay occurs, for example, in thin plasmas at sufficiently high temperatures and in dilute electrolyte solutions, where the correlations are very weaker. For a very thin plasma the ion-ion correlations are very weak and  $\kappa \approx \kappa_{\rm DH}$ , where  $\kappa_{\rm DH}$  is the Debye-Hückel screening parameter that is defined from

$$\kappa_{\rm DH}^2 = \frac{\beta}{\varepsilon_0} \sum_j n_j^b q_j^2, \tag{1}$$

where  $\beta = (k_B T)^{-1}$ ,  $k_B$  Boltzmann's constant, T the absolute temperature,  $\varepsilon_0$  the permittivity of vacuum,  $q_j$  the charge of an ion of species j and  $n_j^b$  the number density of this species (superscript b stands for bulk). The sum is over all species j in the liquid. In an electrolyte solution where the solvent is a dielectric medium with dielectric constant  $\varepsilon_r$ , the expression for the Debye-Hückel parameter is instead given by

$$\kappa_{\rm DH}^2 = \frac{\beta}{\varepsilon_r \varepsilon_0} \sum_j n_j^{\rm b} q_j^2 \quad \text{(in dielectric medium)},$$
(2)

which differs from Eq. (1) by the factor  $\varepsilon_r$  in the denominator. For an electrolyte solution with a solvent consisting of electroneutral molecules,  $\kappa \rightarrow \kappa_{\rm DH}$  in the limit of infinite dilution, where  $\kappa_{\rm DH}$ is given by Eq. (2) with  $\varepsilon_r$  being the dielectric constant of the pure solvent. The same holds for a plasma in the limit of infinitely low density, but with  $\kappa_{DH}$  from Eq. (1). When the density of ions is not very low  $\kappa \neq \kappa_{DH}$  and the decay behavior of the potential for large distances remains plain exponential when the density is increased until the so-called Kirkwood cross-over point is reached, <sup>16</sup> where the decay instead becomes exponentially damped, oscillatory. This cross-over is named after John G. Kirkwood, who was the first to show the existence of oscillatory decay of electrostatic interactions in electrolytes a very long time ago.<sup>17,18</sup> In the oscillatory case there is normally a layering of the ions around a particle or outside a surface into alternating anionrich and cation-rich layers, leading to an oscillation in sign of the charge density and the electrostatic potential - oscillations that extend to large distances (in principle, to infinity).

The free energy of interaction (the potential of mean force) between two particles in an electrolyte has at large separations the same decay length as the electrostatic potential (in the oscillatory case also the same wave length), provided the screened electrostatic interaction dominates for large distances. The same is true for the interactions between two surfaces in contact with the electrolyte. Such interactions can, for example, be measured in surface force experiments as mentioned earlier. The long-ranged monotonic exponential decay that have been observed in some ionic liquids is quite remarkable since these liquids are very dense and the ion-ion correlations are very strong.

It is quite common in the literature that the thinking about screening behavior in electrolytes is based on mean field theories like the Poisson-Boltzmann (PB) approximation and its linearized version the Debye-Hückel (DH) approximation. They predict that  $\kappa$  is equal to  $\kappa_{DH}$  as given by the expressions (1) or (2). A key assumption in these approximations as applied to electrolytes near surfaces is that the ion-ion correlations in the electrolyte outside a surface are entirely neglected.\* This can be a fair approximation for electrolyte solutions that are not too concentrated, but not for ionic liquids where the ion-ion correlations definitely are very important. For conditions in ionic liquids where the density is high, the Debye length  $1/\kappa_{\rm DH}$  is very short. Nevertheless, one could perhaps argue that many ions in an ionic liquid associate forming some complexes, for instance ion pairs, and that the ionic density in Eq. (2) therefore should refer to the remaining "free ions." Thereby,  $\varepsilon_r$  could perhaps mimic a dielectric constant of the associated ions forming a "solvent" for the free ions. The conditions may therefore be reminiscent of dilute electrolyte solutions. However, the PB approximation cannot give an exponentially damped, oscillatory decay and, as we will see, it is not correct to use Eqs. (1) or (2) in order to find the decay length of the plain exponential decay. An understanding of why the electrostatic interaction can have a plain exponential decay instead of an oscillatory decay needs an analysis that includes both decay behaviors.

In this work we analyze electrostatic interactions in systems with ions of arbitrary shape and any internal charge distribution, but we restrict ourselves to cases where the nonelectrostatic interactions are short-ranged and where the screened electrostatic interactions dominate between the constituent particles at large distances. Furthermore, we avoid conditions near critical points. For simplicity we assume that the particles in the electrolyte are rigid and not polarizable. Since we will deal with equilibrium properties we use classical equilibrium statistical mechanics. Under these conditions, the analysis is done without any approximations, so the results are exact.

A major topic in the present paper is the fact that the ionion correlations in dense electrolytes make electrostatics nonlocal, meaning that the ion density at one point is influenced by the electrostatic potential in a whole neighborhood of this point. This applies, for example, to the ion density profiles outside a surface. Mean field theories like the PB approximation assume that the electrostatics is strictly local, i.e., that the density at one point is given solely by the mean electrostatic potential at the same point. They can therefore not properly capture behaviors of the dense electrolytes like ionic liquids.

By exploiting the nonlocality of the electrostatics, we will derive a remarkably simple, but exact expression for the decay parameter  $\kappa$ , that replaces the PB expressions (1) and (2). We will find that<sup>19</sup>

$$\kappa^2 = \frac{\beta}{\mathcal{E}_r^* \varepsilon_0} \sum_j n_j^b q_j q_j^*,\tag{3}$$

where  $\mathcal{E}_r^*$  is a kind of effective dielectric permittivity and  $q_j^*$  is a renormalized charge of the ions of species *j*; a sort of effective charge of the ions. This formula is obviously quite similar to Eq.

<sup>\*</sup> For bulk electrolytes the PB approximation implies that the ion-ion correlations in the ion cloud surrounding each ion are neglected.

(2); the only differences being the occurrence of  $\mathcal{E}_r^*$  instead of  $\varepsilon_r$ and the replacement of one of the factors  $q_j$  by  $q_j^*$ . Note that  $n_j^b$  in Eq. (3) is the total bulk density of ions of species j irrespectively if they are associated or not. Furthermore, the remaining  $q_j$  is the actual charge of a j ion (the bare charge). The deviation of  $q_j^*$ from  $q_j$  and  $\mathcal{E}_r^*$  from the value 1, i.e., the relative permittivity of vacuum, arise from ion-ion correlations. For a thin plasma at high temperatures the correlations are not so important so  $q_j^* \approx q_j$  and  $\mathcal{E}_r^* \approx 1$ , which according to Eq. (1) implies  $\kappa \approx \kappa_{\text{DH}}$  and the PB result is recovered. Likewise, for a dilute electrolyte solution  $q_j^* \approx$  $q_j$  and  $\mathcal{E}_r^* \approx \varepsilon_r$ , the dielectric constant for the solvent. According to Eq. (2) we again have  $\kappa \approx \kappa_{\text{DH}}$ . Otherwise  $\kappa \neq \kappa_{\text{DH}}$  in general.

The two modifications of the expressions for  $\kappa_{\text{DH}}$ , i.e., the appearances of  $q_j^*$  and  $\mathcal{E}_r^*$ , capture, in fact, the behaviors we have discussed above – as they must because Eq. (3) is an exact formula.  $\mathcal{E}_r^*$  is, as we will see, a function of  $\kappa$ , so Eq. (3) is actually an equation for  $\kappa$ . This equation can have both real and complex-valued solutions; real solutions give plain exponential decay and complex solutions give, as will be apparent later, exponentially damped, oscillatory decay. Furthermore, we will see that even for a dense system  $\kappa$  can be real and small, which means that the long-ranged monotonic exponential decay is a possibility for ionic liquids.

The analysis of the statistical mechanics of electrolytes and screened electrostatic surface forces in this paper is done by using an exact formalism, the Dressed Ion Theory (DIT), <sup>20–22</sup> which originally was set up for spherical ions, and its extension Dressed Molecule Theory (DMT), <sup>23–25</sup> that applies to arbitrarily shaped molecules with any internal charge distribution. The systems that are treated in this work consist of electrolytes with immersed planar walls that have arbitrary internal charge distribution. The walls can have any short-ranged ion-surface interaction, so a wide range of internal wall structures are included in the treatment. We will consider ionic liquids or other electrolytes in contact with one surface or located in the slit between two surfaces. In the latter case we assume that there is equilibrium between the liquid in the slit and a bulk liquid of a specified composition. Electroneutral molecules can also be present, like in electrolyte solutions, but the main focus is ionic liquids without solvent.

The treatment presented here is a generalization of DIT for double layer interactions given in our previous work, Ref. 26, which solely considers spherical ions and hard walls with uniform surface charges (see also Refs. 27–30 for this kind of system). Despite that we here extend the theory and treat much more general cases in the current work, the presentation and derivations below are, in fact, much simpler than in our previous work, which is more mathematically involved but at the same time more complete. The simplified version of DIT and DMT of this paper is used in order to make the theory more accessible to nonexperts. Reader who are interested in technical details are referred to the previous work on these theories for complementary aspects.

The screening behavior in bulk electrolytes and the close relationship of this behavior to the dielectric properties of bulk ionic liquids (in particular the static dielectric function) is treated in a separate paper, Ref. 19. That paper also includes a quite detailed analysis of consequences of ionic associations like ion pairing.

The current paper is organized as follows. In Section 2 we start for simplicity with systems containing spherical ions, analyzing nonlocal electrostatics and the polarization response of the electrolyte due to the presence of an immersed wall. An exact equation for  $\kappa$  is derived, which contains the polarization response function of the electrolyte. This equation can alternatively be expressed as in Eq. (3), which gives the link to the expressions for  $\kappa_{\rm DH}$  above. We give conditions for the replacement of oscillatory decay by plain exponential decay in dense electrolytes. In Section 3 we treat the more general case with ions of arbitrary internal charge distributions and shapes. Due to the orientational degrees of freedom of the ions, the treatment is by necessity a bit more complicated than for spherical ions, but the equations for  $\kappa$  and their main consequences remain the same. The DIT concept of a "dressed wall" is generalized to the case of surfaces with any internal charge distribution and any short-ranged ion-surface interactions. The average electrostatic potential due to a wall is given by an analogue to Coulomb's law involving the charge distribution of a dressed wall and the normalized screened Coulomb potential of the bulk electrolyte. Ion-wall interactions and surface forces between two planar walls are analyzed and the concept of effective surface charge density is introduced for the general case. The relationship between the effective surface charge density and the dress of the wall is derived. It is shown that the magnitude of the screened electrostatic surface interaction for large separations is proportional to the product of the effective surface charge densities of the walls. The decay behavior of this interaction is of the same type as in the bulk liquid. In Section 4 the conclusions of the paper are summarized. Finally, Appendix A gives details regarding decay of the electrostatic potential from a planar wall with arbitrary internal charge distribution.

#### 2 Electrolytes with spherical ions

In this section we will treat electrolytes consisting of spherical anions and cations with point charge at the center of the sphere. Consider a single planar wall in contact with a bulk electrolyte with composition specified by densities  $n_i^b$  for the various species j. We select a coordinate system with the z axis perpendicular to the wall and denote a coordinate point as  $\mathbf{r} = (x, y, z)$ . The wall has an internal charge density  $\sigma_w(\mathbf{r})$ , which may be a continuous distribution or consist of a set of point charges spread both inside the wall and on its surface. A special case is a smooth hard wall with a uniformly smeared out sheet of charge with surface density  $\sigma^{S}$ , i.e.,  $\sigma_{w}(\mathbf{r}) = \sigma^{S} \delta(z)$ , where  $\delta(z)$  is the one-dimensional Dirac function. Here we have placed the coordinate system with origin at the sheet of surface change. We will, however, start with the general case. Ions of species j interact with the wall via a short-ranged, but otherwise arbitrary interaction potential  $v_i^{sh}(\mathbf{r})$ in addition to the electrostatic interactions with the charge density  $\sigma_w(\mathbf{r})$  inside the wall.

Due to the interactions between the surface and the ions, the ionic number densities deviate from the bulk values in the neighborhood of the surface. The number density of ions of species j at coordinate **r** is equal to

$$n_j(\mathbf{r}) = n_j^{\mathrm{b}} e^{-\beta W_j(\mathbf{r})},\tag{4}$$

$$\rho_{w}(\mathbf{r}) = \sum_{j} q_{j} n_{j}^{b} e^{-\beta W_{j}(\mathbf{r})}.$$
(5)

The varying ion densities outside the surface is often described as an "ion cloud" with charge density  $\rho_w(\mathbf{r})$ . When  $z \to \infty$  we have  $n_j(\mathbf{r}) \to n_j^{\rm b}$  and  $\rho_w(\mathbf{r}) \to 0$ .

The mean electrostatic potential is given by Coulomb's law as

$$\psi_w(\mathbf{r}_2) = \int d\mathbf{r}_1 \left[ \sigma_w(\mathbf{r}_1) + \rho_w(\mathbf{r}_1) \right] \phi_{\text{Coul}}(r_{12}) + \text{ const.}, \quad (6)$$

where  $r_{12} = |\mathbf{r}_{12}|$ ,  $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ ,  $\phi_{\text{Coul}}(r) = 1/(4\pi\varepsilon_0 r)$  and const. is selected such that  $\psi_w(\mathbf{r}_2) \to 0$  when  $z_2 \to \infty$ . The integration is taken over the whole space (all integrations without explicit limits in this paper are taken over all possible values of the respective variables). The potential  $\psi_w$  satisfies Poisson's equation

$$-\varepsilon_0 \nabla^2 \psi_w(\mathbf{r}) = \sigma_w(\mathbf{r}) + \rho_w(\mathbf{r})$$
(7)

with boundary condition  $\psi_w(\mathbf{r}) \to 0$  when  $z \to \infty$  and where  $\nabla^2$  denotes the Laplace operator.

# 2.1 Nonlocal electrostatics and polarization response in the tail region

In the Poisson-Boltzmann approximation it is assumed that the density of *j* ions at any coordinate **r** is solely determined by the electrostatic potential  $\psi_w$  at the same coordinate; in other words one assumes that there is an *entirely local electrostatics*. We then have

$$W_j(\mathbf{r}) = q_j \psi_w(\mathbf{r}) \quad \text{(PB)}, \tag{8}$$

where (PB) means that the equation is valid only in the PB approximation. In actual fact, the average density of *j* ions at point **r** is affected by the values of electrostatic potential  $\psi_w$  in a whole neighborhood of this point. Consider ions at various coordinates **r'** around the point **r**. They interact with the electrostatic potential and since they influence, via ion-ion correlations, the probability for ions to be at **r**, the density at **r** is affected by the potential at all points **r'**. Thus, in reality there is *nonlocal electrostatics*. This is particularly important for ionic liquids since the density is very high and the ion-ion correlations are large.

We will first consider the situation for large *z*, i.e., in the tails of  $W_j(\mathbf{r})$  and  $\rho_w(\mathbf{r})$  far from the wall surface where the electrostatic potential due to the surface is weak, and see how the ionion correlations can be properly included there. For simplicity we restrict ourselves throughout this paper to cases where all interactions apart from the electrostatic ones are short-ranged, so the electric field due to the wall and its ion cloud constitutes the longest range effect in  $W_j(\mathbf{r})$  and therefore determines the leading contribution to the tail of this function.<sup>†</sup> As we have seen, the ion density  $n_j(\mathbf{r})$  at coordinate  $\mathbf{r}$  depends on the potential  $\psi_w$  in an entire neighborhood of this coordinate. The same must apply for  $W_j(\mathbf{r})$  since  $\beta W_j(\mathbf{r}) = -\ln[n_j(\mathbf{r})/n_j^b]$  as follows from Eq. (4). In mathematical terms, this means that  $W_j$  is a *functional* of  $\psi_w$ . When z is sufficiently large and  $\psi_w(\mathbf{r})$  therefore is small, we are in the linear response regime, which implies that  $W_j$  is a *linear* functional of  $\psi_w$ . This implies that we have

$$W_j(\mathbf{r}) = \int d\mathbf{r}' \psi_w(\mathbf{r}') \rho_j^*(|\mathbf{r} - \mathbf{r}'|), \quad \text{(weak field)}, \qquad (9)$$

where the function  $\rho_j^*$  is not yet known. (The existence and uniqueness of such a function follow from Rietz' representation theorem for linear functionals.<sup>31</sup> This means that Eq. (9) is exact in the limit  $z \to \infty$ .) The entity  $\rho_j^*$  has the physical role of an "effective" charge density associated with the *j* ion and the integral is the electrostatic energy of interaction between  $\rho_j^*$  and  $\psi_w$ . Note that the expression (9) implies that the value of  $W_j$  at coordinate **r** is affected by the values of  $\psi_w$  at various points **r'** via the factor  $\rho_j^*(|\mathbf{r} - \mathbf{r'}|)$ , which is nonzero for range of  $|\mathbf{r} - \mathbf{r'}|$  values. In contrast to this, in the PB approximation, Eq. (8), one simply has replaced  $\rho_j^*(\mathbf{r})$  with  $q_j \delta^{(3)}(r)$  in Eq. (9), where  $\delta^{(3)}(r)$  is the three-dimensional Dirac delta function. This highlights the local electrostatics in this approximation. Note also that  $\rho_j^*$  in the general case describes linear response due to  $\psi_w$  and is a property of the unperturbed bulk electrolyte.

The entity  $\rho_j^*$  is, in fact, the charge density of a so-called *dressed* ion in DIT, <sup>20–22,26</sup> where this concept is defined in a different and quite formal manner. The role of  $\rho_j^*$  as an effective charge density in the interaction with the mean potential described above, is just one of its several roles in electrolyte theory (more will be described later). Let us consider this particular role a bit further. A dressed ion consists of the ion itself and a "dress", which is a charge density surrounding the ion and associated with it:

$$\rho_{j}^{*}(r) = q_{j} \delta^{(3)}(r) + \rho_{j}^{\text{dress}}(r), \qquad (10)$$

where r is the distance from the ion center. The first term on the right hand side (rhs) is the bare charge of the j ion (i.e., the point charge at the center) expressed as a charge density and the second term is the dress. By inserting Eq. (10) into Eq. (9), the latter becomes

$$W_j(\mathbf{r}) = q_j \psi_w(\mathbf{r}) + \int d\mathbf{r}' \psi_w(\mathbf{r}') \rho_j^{\text{dress}}(|\mathbf{r} - \mathbf{r}'|), \quad \text{(weak field)}.$$
(11)

The first contribution is the interaction between the potential  $\psi_w$  and the bare charge  $q_j$  of the ion and in the second term  $\rho_j^{\text{dress}}$  takes care of effects of ion-ion correlations in the interaction of the *j* ion with  $\psi_w$  when the latter is small as described earlier.

Some further features of a dressed ion can be explained as follows. An ion in the bulk electrolyte is surrounded by an ion cloud of charge density  $\rho_j(r)$ , which has a total charge that is of opposite sign to  $q_j$  and neutralizes the latter,  $\int d\mathbf{r} \rho_j(r) = -q_j$  (the condition of local electroneutrality). The dress  $\rho_j^{dress}(r)$  is a *part* of the charge density  $\rho_j(r)$ , is in general more short-ranged than  $\rho_j(r)$ , and can be calculated from the pair distribution functions of the bulk electrolyte. <sup>19,20,32</sup> Since the dress is only a part of  $\rho_j$ , we have in general  $\int d\mathbf{r} \rho_j^{dress}(r) \neq -q_j$ , which implies that  $q_i^* \equiv \int d\mathbf{r} \rho_i^*(r) \neq 0$ . Thus the total charge  $q_i^*$  of the dressed ion

 $<sup>\</sup>dagger$  The general DIT and DMT formalisms  $^{20,22,23,25,26}$  can be applied to other cases, but the simplified version used here has this limitation.

is generally nonzero, but it may, however, change sign, which means that it can fortuitously be equal to zero for some states of the system.

Let us now consider the charge density of the ion cloud outside the wall given by  $\rho_w$  in Eq. (5). For large *z* where  $W_j(\mathbf{r})$  is small, we can replace  $\exp[-\beta W_j(\mathbf{r})]$  by  $1 - \beta W_j(\mathbf{r})$ . By introducing this in Eq. (5), inserting Eq. (9) and using the fact that  $\sum_j q_j n_j^b = 0$  due to electroneutrality, we obtain

$$\rho_{w}(\mathbf{r}) \sim -\beta \sum_{j} q_{j} n_{j}^{b} \int d\mathbf{r}' \psi_{w}(\mathbf{r}') \rho_{j}^{*}(|\mathbf{r} - \mathbf{r}'|)$$
$$= \int d\mathbf{r}' \psi_{w}(\mathbf{r}') \chi^{*}(|\mathbf{r} - \mathbf{r}'|), \quad z \to \infty, \qquad (12)$$

where the symbol  $\sim$  means "decays asymptotically as" and we have defined

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

Eq. (12) says that the function  $\chi^*$  determines the charge density  $\rho_w$  due to the potential  $\psi_w$  in the linear regime, i.e., for small  $\psi_w$ . When  $\psi_w$  is zero, the electrolyte is in its bulk state and the effect of nonzero  $\psi_w$  is to polarize the electrolyte. The charge density  $\rho_w$  for large *z* is the polarization response of the bulk electrolyte due to the potential  $\psi_w$ , implying that  $\chi^*$  is a *polarization response function* in linear response theory. Note that  $\chi^*$  is a property of the bulk electrolyte.

In the PB approximation we have when  $z \rightarrow \infty$ 

$$\begin{split} \rho_w(\mathbf{r}) &\sim -\beta \sum_j q_j n_j^{\rm b} \int d\mathbf{r}' \psi_w(\mathbf{r}') q_j \delta^{(3)}(|\mathbf{r} - \mathbf{r}'|) \\ &= -\beta \sum_j n_j^{\rm b} q_j^2 \psi_w(\mathbf{r}) \quad \text{(PB)}, \end{split}$$

so the polarization response function is given by

$$\chi^{*}(r) = -\beta \sum_{j} n_{j}^{b} q_{j}^{2} \delta^{(3)}(r) = -\varepsilon_{0} \kappa_{\rm DH}^{2} \delta^{(3)}(r) \quad (\text{PB}), \tag{14}$$

where  $\kappa_{DH}$  is the Debye-Hückel screening parameter. As before, the local electrostatics in the PB approximation is expressed by a delta function; here it occurs in  $\chi^*$ .

#### 2.2 The decay length for the electrostatic potential

Let now consider the special case of a smooth hard wall with a uniformly smeared out surface charge density  $\sigma^S$ . Then  $n_j$ ,  $W_j$ ,  $\rho_w$ , and  $\psi_w$  depend on the coordinate *z* only. In the PB approximation we have the well-known fact that the potential  $\psi_w(z)$  decays when  $z \to \infty$  as

$$\psi_w(z) \sim A_w^{\mathrm{PB}} e^{-\kappa_{\mathrm{DH}} z}$$
 (PB),

where  $A_w^{\text{PB}}$  is a constant. For the general, exact case it has been shown<sup>26</sup> that we have the same kind of decay for the potential, but with a different pre-factor  $A_w$  and decay parameter  $\kappa$ , that is,

$$\Psi_w(z) \sim A_w e^{-\kappa z} \quad z \to \infty$$
 (15)

provided the electrostatic coupling is sufficiently weak. Thus, the decay length  $\lambda = \kappa^{-1}$  differs from the Debye length  $\lambda_{DH} = \kappa_{DH}^{-1}$ .

When the coupling is stronger, this kind of decay is replaced by an oscillatory, exponentially decaying one

$$\psi_w(z) \sim B_w \cos(\kappa_{\mathfrak{F}} z + \vartheta_w) e^{-\kappa_{\mathfrak{F}} z}, \qquad (16)$$

where  $B_w$  is a constant,  $\vartheta_w$  is a phase shift and where  $\kappa_{\Re}$  and  $\kappa_3$  are the decay parameter and wave number, respectively, for the decay. The decay length is  $\lambda = 1/\kappa_{\Re}$  and the wave length is  $2\pi/\kappa_3$ . The quantities  $\kappa_{\Re}$  and  $\kappa_3$  can, as we shall see, be regarded as the real and imaginary parts of  $\kappa = \kappa_{\Re} + i\kappa_3$ , where i is the imaginary unit (distinguish i from the species index *i*), and the oscillatory behavior in Eq. (16) is then included in Eq. (15). As mentioned earlier, oscillatory decay occurs, for example, in molten simple salts and many ionic liquids. Such a decay can, of course, not be obtained in the PB approximation where  $\kappa = \kappa_{\rm DH}$  is always real.

Now, let us derive an exact equation for the decay parameter  $\kappa$ . In the rhs of the Poisson equation (7) the charge density  $\sigma_w(\mathbf{r})$  is zero outside the wall and  $\rho_w(\mathbf{r})$  decays according to Eq. (12). Far from the wall we therefore obtain from the Poisson equation

$$-\varepsilon_0 \frac{d^2 \psi_w(z)}{dz^2} \sim \int d\mathbf{r}' \psi_w(z') \boldsymbol{\chi}^*(|\mathbf{r} - \mathbf{r}'|), \quad z \to \infty.$$
(17)

By inserting the limiting form (15) of  $\psi_w(z)$  on both sides and performing the derivative in the left hand side (lhs), we obtain for large z

$$-\varepsilon_{0}\kappa^{2}A_{w}e^{-\kappa z} \sim \int d\mathbf{r}'A_{w}e^{-\kappa z'}\chi^{*}(|\mathbf{r}-\mathbf{r}'|)$$
$$= \int dr''(r'')^{2}\left[\int d\mathbf{\hat{r}}''A_{w}e^{-\kappa(z-z'')}\right]\chi^{*}(r''), (18)$$

where the last equality follows after a variable substitution  $\mathbf{r}'' = \mathbf{r} - \mathbf{r}'$  and where the radial integration over r'' in spherical polar coordinates and the integration over the angles have been separated. These angles are represented by the unit vector  $\mathbf{\hat{r}}'' = \mathbf{r}''/r''$ .

We now break out a factor  $A_w \exp(-\kappa z)$  from the square bracket in the rhs of Eq. (18) and use the fact that

$$\int d\mathbf{\hat{r}}^{\prime\prime} e^{\kappa z^{\prime\prime}} = 4\pi \frac{\sinh(\kappa r^{\prime\prime})}{\kappa r^{\prime\prime}},$$

whereby we obtain from Eq. (18)

$$-\varepsilon_0 \kappa^2 A_w e^{-\kappa_z} \sim 4\pi A_w e^{-\kappa_z} \int dr'' (r'')^2 \frac{\sinh(\kappa r'')}{\kappa r''} \chi^*(r'').$$
(19)

By identifying the coefficients on either side we obtain after simplification

$$-\varepsilon_0 \kappa^2 = \int d\mathbf{r}'' \frac{\sinh(\kappa r'')}{\kappa r''} \chi^*(r''), \qquad (20)$$

where  $d\mathbf{r}'' = dr''(r'')^2 4\pi$  (spherical symmetry). This relationship is an equation<sup>‡</sup> for the unknown variable  $\kappa$ . For a given function

<sup>‡</sup> This equation for  $\kappa$  can be expressed in various equivalent forms, including the new relationship (3) that is proven later in this work and the expression mentioned in the next footnote §. Other equivalent equations for  $\kappa$  include expressions that contain the Fourier transform  $\tilde{c}_{ij}(k)$  of the direct correlation functions  $c_{ij}(r)$  like in Refs. 16,22,29. The latter expressions can be written in terms of the static dielectric

 $\chi^*$ , the equation can be used to determine  $\kappa$ , at least numerically. The function  $\chi^*$  is independent of  $\kappa$  but is, of course, dependent on the state of the system.

By inserting Eqs. (10) and (13) into Eq. (20) we obtain<sup>§</sup>

$$\kappa^{2} = \frac{\beta}{\varepsilon_{0}} \sum_{j} n_{j}^{b} q_{j} \left[ q_{j} + \int d\mathbf{r} \frac{\sinh(\kappa r)}{\kappa r} \rho_{j}^{dress}(r) \right]$$
$$= \kappa_{\rm DH}^{2} + \frac{\beta}{\varepsilon_{0}} \sum_{j} n_{j}^{b} q_{j} \int d\mathbf{r} \frac{\sinh(\kappa r)}{\kappa r} \rho_{j}^{dress}(r).$$
(21)

Thus, the presence of the last term, which arises because of ionion correlations and the resulting nonlocal electrostatics, makes  $\kappa \neq \kappa_{\rm DH}$ . In the limit  $n_j^b \rightarrow 0$  for all *j*, i.e., for a thin plasma in the limit of zero density, we have  $\kappa \sim \kappa_{\rm DH} \rightarrow 0$  so the Debye-Hückel result is recovered in this limit – a well-known result (this is due to the fact<sup>20</sup> that the integral goes to zero like  $\kappa$ , so last term goes to zero faster than  $\kappa_{\rm DH}^2$  when the density goes to zero).

Equation (20) has in general several solutions  $\kappa$ . Each solution gives rise to a term in  $\psi_w$  like that in Eq. (15) with the respective  $\kappa$  value inserted. Thus, there are several such terms with different decay lengths.<sup>¶</sup> By including the two leading terms, we have<sup>30</sup>

$$\psi_w(z) \sim A_w e^{-\kappa z} + A'_w e^{-\kappa' z}, \quad z \to \infty,$$
(22)

where both  $\kappa$  and  $\kappa'$  are solutions to Eq. (20) and where  $A_w$  and  $A'_w$  are constants. The  $\kappa$  value we have discussed earlier is the solution that corresponds to the leading decay of  $\psi_w$  for large *z*, i.e., the term with the longest decay length (i.e., the smallest  $\kappa$  value).

Solutions to Eq. (20) are not necessarily real-valued; also complex-valued solutions exist in general. In some cases the leading solution (with the longest decay length) is complex-valued and we obtain the oscillatory, exponentially decaying behavior shown in Eq. (16). For a complex-valued solution, say  $\kappa = \kappa_{\Re} + i\kappa_{\Im}$  with real  $\kappa_{\Re}$  and  $\kappa_{\Im}$ , the complex conjugate  $\kappa_{\Re} - i\kappa_{\Im}$  is also a solution to Eq. (20), so we have  $\kappa' = \kappa_{\Re} - i\kappa_{\Im}$  and Eq. (22) applies. The prefactors  $A_w$  and  $A'_w$  are, in fact, complex-valued too (complex conjugates)  $A_w = |A_w| \exp(-i\vartheta_w)$  and  $A'_w = |A'_w| \exp(i\vartheta_w)$ , where  $\vartheta_w$  is a real number and  $|A_w| = |A'_w| = B_w/2$ , which defines  $B_w$ . This implies that the sum of the two terms in Eq. (22) is a

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real valued function (as it must for physical reasons)

$$\begin{split} \Psi_{w}(z) &\sim |A_{w}|e^{-\mathrm{i}\vartheta_{w}}e^{-(\kappa_{\Re}+\mathrm{i}\kappa_{\Im})z} + |A'_{w}|e^{\mathrm{i}\vartheta_{w}}e^{-(\kappa_{\Re}-\mathrm{i}\kappa_{\Im})z} \\ &= \frac{B_{w}}{2}\left[e^{-\mathrm{i}(\kappa_{\Im}z+\vartheta_{w})} + e^{\mathrm{i}(\kappa_{\Im}z+\vartheta_{w})}\right]e^{-\kappa_{\Re}z} \\ &= B_{w}\cos(\kappa_{\Im}z+\vartheta_{w})e^{-\kappa_{\Re}z}, \end{split}$$
(23)

which it is equal to the expression in Eq. (16).

Cross-over from plain exponential to oscillatory, exponentially decaying behavior occur, as mentioned earlier, when the ionic density of a high-temperature plasma increases from a small to a large value.<sup>15,16</sup> Such cross-overs can also occur in ionic liquids when conditions are changed. Consider a system with plain exponential decay where we have two leading terms as in Eq. (22) with real-valued  $\kappa$ ,  $\kappa'$ ,  $A_w$  and  $A'_w$  and with  $\kappa < \kappa'$  (recall that both  $\kappa$  and  $\kappa'$  are solutions to Eq. (20)). The first term accordingly has a larger decay length than the second and gives the leading decay. At the cross-over point to oscillatory behavior, the two solutions  $\kappa$ and  $\kappa'$  merge and become two complex-valued solutions that are each other's complex conjugate (just like the behavior of the solutions of, for example, a quadratic equation with real coefficients; those solutions can change between real and complex-valued in this manner when the coefficients are varied). Then the decay in Eq. (22) changes to that in Eq. (16). This behavior of the decay is nicely illustrated in the molecular-dynamics simulations for plasmas and molten salts by Keblinski et al.<sup>15</sup>

When the decay is oscillatory, there is a layering of the ions outside a surface into alternating anion-rich and cation-rich layers, which, as pointed out earlier, leads to the oscillation in sign of the charge density and the electrostatic potential. This layering extends far out into the liquid (in principle to infinity, but it is of course not noticeable after several multiples of the decay length  $\lambda$ ). There also exists cases where there are some oscillations at small z close to the surface, but where the decay turns into a plain exponential one at larger *z* and remains exponential when  $z \rightarrow \infty$ . The decay that we have discussed above is the ultimate kind of decay for sufficiently large z. What is sufficient for this ultimate decay to take over is system-dependent; in many cases the distance need not be very large 15,32 (it can be as short as a couple of ionic diameters in some cases). Whether this decay is plain exponential or exponentially damped oscillatory is determined by the bulk properties of the ionic liquid. Thereby, the same values of decay parameters ( $\kappa$  or  $\kappa_{\Re}$  and  $\kappa_{\Im}$ ) apply for the electrostatic interactions between all particles of the system and between the particles and the surface (and, as we shall see, between two surfaces at sufficiently large separations from each other). On the other hand, specific properties of individual surfaces lie behind the occurrence of some oscillations at small distances from a surface in cases when the ultimate decay is plain exponential. Such oscillations can exist for one surface in contact with the ionic liquid but not necessarily for another surface in contact with the same liquid.

function  $\tilde{e}(k)$  as explained in Section IV of Ref. 22, where the equation for  $\kappa$  is D(k) = 0 with  $k = i\kappa$  and D is a determinant containing  $\tilde{c}_{ij}(k)$ . It is shown in Ref. 22 that  $D(i\kappa) = 0$  implies  $\tilde{e}(i\kappa) = 0$  for the cases that are relevant for the electrostatic potential (other solutions of D(k) = 0 solely affect the decay behavior of the density distribution). Since  $\tilde{e}(k) = 1 - \tilde{\chi}^*(k) \tilde{\phi}_{Coul}(k)$  one can reformulate the equation  $\tilde{e}(i\kappa) = 0$  as Eq (20). The route we use for obtaining Eq (20) in the present work is *much* simpler.

<sup>§</sup> Equation (21) can be expressed as  $\kappa^2 = \beta \sum_j n_j^{\rm b} q_j q_j^{\rm eff} / \epsilon_0$ , where  $q_j^{\rm eff} = \int d\mathbf{r} \rho_j^*(r) \sinh(\kappa r) / (\kappa r)$ , see Refs. 20,21 where  $q_j^{\rm eff}$  is denoted  $q_j^*$  (the latter is thus different from  $q_j^*$  in the current paper). This appealing expression for  $\kappa^2$  is, however, only applicable for spherical ions. In contrast to this, Eq. (3) is valid in general as will be demonstrated in Section 3.

<sup>¶</sup> There are also terms in the decay that have a different functional forms.<sup>20,22,32</sup> In the cases considered here these terms have shorter decay lengths.

as

#### 2.3 Alternative equation for $\kappa$

Let us now investigate the equation for  $\kappa$ , Eq. (20), a bit further. We can, in fact, write it as Eq. (3). To this end, we write the former equation as

$$-\varepsilon_{0}\kappa^{2} = \int d\mathbf{r} \frac{\sinh(\kappa r)}{\kappa r} \chi^{*}(r)$$
$$= \int d\mathbf{r} \chi^{*}(r) + \kappa^{2} \int d\mathbf{r} r^{2} \left[ \frac{\sinh(\kappa r) - \kappa r}{(\kappa r)^{3}} \right] \chi^{*}(r) \quad (24)$$

(note that the square bracket remains finite when  $\kappa r \rightarrow 0$ ). By moving the last integral to the lhs we can express this equation as

$$-\varepsilon_0 \kappa^2 \mathcal{E}_r^* = \int d\mathbf{r} \boldsymbol{\chi}^*(r), \qquad (25)$$

where we have defined

$$\mathcal{E}_{r}^{*} = 1 + \frac{1}{\varepsilon_{0}} \int d\mathbf{r} r^{2} \left[ \frac{\sinh(\kappa r) - \kappa r}{(\kappa r)^{3}} \right] \chi^{*}(r).$$
(26)

By using the definition of  $\chi^*$ , Eq (13), we have

$$\int d\mathbf{r} \boldsymbol{\chi}^*(r) = -\beta \sum_j q_j n_j^{\rm b} \int d\mathbf{r} \boldsymbol{\rho}_j^*(r) = -\beta \sum_j n_j^{\rm b} q_j q_j^*, \qquad (27)$$

where

$$q_j^* = \int d\mathbf{r} \boldsymbol{\rho}_j^*(r)$$

is the total charge of the dressed ion. As we saw earlier, we have in general  $q_j^* \neq 0$ . By introducing Eq. (27) into Eq. (25) we finally obtain Eq. (3), that is,

$$\kappa^2 = \frac{\beta}{\mathcal{E}_r^* \varepsilon_0} \sum_j n_j^b q_j q_j^*.$$
 (28)

The similarity between this formula and Eq. (2) is obvious. The quantity  $\mathcal{E}_r^*$  plays the role as an effective relative permittivity of the electrolyte. Note that Eq. (28) is an equation for  $\kappa$  since the rhs depends on  $\kappa$  via  $\mathcal{E}_r^*$ . The dressed ion charge  $q_j^*$  is independent of the parameter  $\kappa$  (but  $q_j^*$  depends, of course, on the state of the system).

For the Debye-Hückel parameter  $\kappa_{DH}$  given by Eq. (1), the only possibility at moderate temperatures for it to be small and hence the Debye length large is that the ion density is small, like in a thin plasma. For the actual screening parameter  $\kappa$  there are other possibilities. A very important difference between the exact equation (28) and the DH formulas is the appearance of the dressed ion charge  $q_j^*$  (in  $n_j^b q_j q_j^*$ ) instead of the bare charge  $q_j$  (in  $n_j^b q_j q_j$ ). Let us consider an ionic liquid with one species of anions and one of cations. As we have seen,  $q_j^*$  includes the charges in the dress and when there is a substantial association between anions and cations, the charge of the dress can have a magnitude that is nearly the same as the bare charge  $q_j$ , but of opposite sign. This means that  $q_+^*$  and  $q_-^*$  can be small, which, as we will see, makes  $\kappa$  small despite that the ion density is high. To verify this we write the effective relative permittivity  $\mathcal{E}_r^* = \mathcal{E}_r^*(\kappa)$  in Eq. (26)

$$\mathcal{E}_{r}^{*}(\kappa) = 1 + \frac{1}{3!\varepsilon_{0}} \int d\mathbf{r} r^{2} \chi^{*}(r) + \frac{\kappa^{2}}{\varepsilon_{0}} \int d\mathbf{r} r^{4} \left[ \frac{\sinh(\kappa r) - \kappa r - (\kappa r)^{3}/3!}{(\kappa r)^{5}} \right] \chi^{*}(r), \quad (29)$$

where the square bracket remains finite when  $\kappa r \rightarrow 0$ . We can express this equation as

$$\mathcal{E}_r^*(\kappa) = \mathcal{E}_r^*(0) + \mathcal{O}(\kappa^2),$$

where

$$\mathcal{E}_r^*(0) = 1 + \frac{1}{6\varepsilon_0} \int d\mathbf{r} r^2 \boldsymbol{\chi}^*(r)$$

(the symbol  $\mathcal{O}(\kappa^2)$  means  $\kappa^2$  times a function that stays finite when  $\kappa \to 0$ ). Thus, Eq. (25) can be written

$$\varepsilon_0 \kappa^2 \left( \mathcal{E}_r^*(0) + \mathcal{O}(\kappa^2) \right) = \beta \sum_j n_j^b q_j q_j^*,$$

so when  $q_{+}^{*}$  and  $q_{-}^{*}$  are small we have (in the limit when both go to zero)

$$\kappa^2 \sim \frac{\beta}{\mathcal{E}_r^*(0)\varepsilon_0} \sum_j n_j^{\mathrm{b}} q_j q_j^*,$$

which implies that  $\kappa$  is small when  $q^*_+$  and  $q^*_-$  are sufficiently small. If  $\mathcal{E}^*_r(0)$  is large,  $\kappa$  can be small even if  $q^*_+$  and  $q^*_-$  are not *very* small. We conclude that the nonlocal electrostatics caused by the strong correlations in an ionic liquid can make  $\kappa$  small (and hence decay length large) despite that the liquid has a large density.  $\mathcal{E}^*_r(0)$  as well as the contributions from the last integral in Eq. (29) contain very important contributions from ion-ion correlations, as can be realized by inserting the expression for  $\chi^*(r)$  in terms of the dressed ion charge densities (Eq. (13) in the present case). This is explored in detail in Ref. 19.

In cases where transient ion pairs are formed in the ionic liquid, it is shown in Ref. 19 that there are contributions to  $\mathcal{E}_r^*$  that correspond to those from dipolar particles (like a dumbbell formed by an anion and a cation of the same valency). When there is a lot of ion pairing,  $q_{+}^{*}$  and  $q_{-}^{*}$  are small since each pair forms an electroneutral entity and since  $q_i^*$  for each *j* is an average over all ions of species *j*, both paired and unpaired, and the latter are in a minority. However, it is not necessary to have an actual pairing to obtain small  $q_+^*$ ,  $q_-^*$  and  $\kappa$ . Small  $\kappa$  values can be encountered when each ion on average is surrounded by several ions of opposite sign that are attracted strongly to the ion for various reasons, for instance ion-ion correlation effects - a more general kind of ion association than pairing. This is a situation that readily can occur in dense ionic liquids. Another possibility is, of course, some nonelectrostatic attraction between anions and cations. A strongly asymmetric distribution of charges in the ions, like a positive patch on one species and a negative on the other, can also favor association.

As briefly discussed in the Introduction, one possibility could perhaps be to consider the associated ions (for whatever reason they are associated) as a "solvent" for the rest of the ions, the "free" ions. Thereby one might apply the DH formula for electrolyte solutions, Eq. (2), and thereby try to mimic  $\mathcal{E}_r^*$  for the ionic liquids by using  $\varepsilon_r$  as a kind of parameter that models the dielectric properties of associated ions. The values of  $n_j^b$  could then modified to instead measure the effective densities of "free" ions. This is, however, fundamentally incorrect since the exact formula (28) contains the dressed ion ions charges,  $q_j^*$ , rather than the bare ones,  $q_j$ . One may argue that the ratio  $q_j/\varepsilon_r$  can be used as a fitting parameter in Eq. (2) that replaces  $q_j^*/\mathcal{E}_r^*$  in the correct formula, but the effect of, for instance, ion-ion correlations on  $q_+^*$  is in general different from the effects on  $q_-^*$ . Therefore, to use a common denominator  $\mathcal{E}_r^*$  in the fitting is fundamentally flawed. In an approximate modeling of ionic liquids one should hence not use classical mean field theories like the DH and PB approximations with fitting parameters, but instead focus on an essentially correct treatment of nonlocal electrostatics and make calculations for entities like  $q_+^*$ ,  $q_-^*$  and  $\mathcal{E}_r^*$ .

The conclusions in this subsection are, in fact, valid also for ions that are not spherical since, as we will see in the next section, Eqs. (20) and (28) are general results that apply for ionic liquids where the ions have arbitrary shapes and internal charge distributions.

### 3 lons with arbitrary internal charge distributions and shapes

We will now generalize the results above to ionic liquids consisting of ions of any shape and any internal charge distribution. For simplicity, we will, however, limit ourselves to rigid ions that are not polarizable. Thereafter, we consider the full polarization of an ionic liquid due to the presence of a wall and investigate in more detail the interaction between a wall and ions in the liquid. Finally, we treat electrostatic interactions between two walls and surface forces. Ionic liquids constitute the main subject of our investigation, but the analysis is valid also for electrolyte solutions with a molecular polar solvent.

First, let us introduce some notations. The internal charge distribution of an ionic or polar particle can be a continuous density or a set of point charges (defined by a set of delta functions). This charge distribution is denoted  $\sigma_j(\mathbf{r}, \omega)$  for a particle of species *j*, where  $\mathbf{r}$  is counted from the center of mass of the particle and  $\omega$  defines the particle's orientation as described by the three Euler angles  $(\varphi, \theta, \eta)$  in the laboratory frame. In general all three angles are needed, but for a linear particle only the azimuthal and polar angles  $(\varphi, \theta)$  are required because the third angle,  $\eta$ , is selected as the redundant rotation around the axis of symmetry. The orientational coordinate that we use equals  $\omega = (\varphi, \cos \theta, \chi)/(8\pi^2)$  for nonlinear particles and  $\omega = (\varphi, \cos \theta)/(4\pi)$  for linear ones; both have the property  $\int d\omega = 1$ .

The total charge of a particle of species j is

$$q_j = \int d\mathbf{r} \boldsymbol{\sigma}_j(\mathbf{r}, \boldsymbol{\omega}), \qquad (30)$$

which, of course, is independent of  $\omega$ , and the dipole moment of the particle is given by

$$\mu_j(\boldsymbol{\omega}) = \int d\mathbf{r} \, \mathbf{r} \sigma_j(\mathbf{r}, \boldsymbol{\omega}). \tag{31}$$

Higher order moments can be defined in a similar manner.

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$$v_j(\mathbf{r}_1,\boldsymbol{\omega}_1) = v_j^{\mathrm{sh}}(\mathbf{r}_1,\boldsymbol{\omega}_1) + v_j^{\mathrm{el}}(\mathbf{r}_1,\boldsymbol{\omega}_1),$$

where  $v_j^{\text{sh}}$  is an arbitrary short-ranged interaction potential and the electrostatic interaction is given by

$$v_j^{\text{el}}(\mathbf{r}_1, \boldsymbol{\omega}_1) = \int d\mathbf{r}_2 d\mathbf{r}_3 \sigma_w(\mathbf{r}_2) \phi_{\text{Coul}}(r_{23}) \sigma_j(\mathbf{r}_{13}, \boldsymbol{\omega}_1).$$
(32)

The pair interaction potential between two particles of species *i* and *j* placed at  $\mathbf{r}_1$  and  $\mathbf{r}_2$  and with orientations  $\omega_1$  and  $\omega_2$ , respectively, is

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

where  $u_{ij}^{sh}$  is the nonelectrostatic interaction and

$$u_{ij}^{\text{el}}(\mathbf{r}_{12},\boldsymbol{\omega}_1,\boldsymbol{\omega}_2) = \int d\mathbf{r}_3 d\mathbf{r}_4 \sigma_i(\mathbf{r}_{13},\boldsymbol{\omega}_1) \phi_{\text{Coul}}(r_{34}) \sigma_j(\mathbf{r}_{24},\boldsymbol{\omega}_2), \quad (33)$$

Like before we assume that the nonelectrostatic interactions are sufficiently short ranged, so the screened electrostatic interactions in the liquid dominate at large distances. Otherwise,  $u_{ij}^{sh}$  is arbitrary (but it must, of course, be strongly repulsive when the ions overlap significantly).

#### 3.1 Polarization response, tail region

Due to the interactions with the wall, the electrolyte outside the surface is inhomogeneous and the particles have an anisotropic distribution of orientations there. The number density for species j is  $n_j(\mathbf{r}, \omega)$ , which means that  $n_j(\mathbf{r}, \omega) d\mathbf{r} d\omega$  is the average number of j particles with orientation within  $d\omega$  around  $\omega$  and with centers in the volume element  $d\mathbf{r}$  around the coordinate  $\mathbf{r}$ . We have  $n_j(\mathbf{r}, \omega) \rightarrow n_j^{\rm b}$  when  $z \rightarrow \infty$ . The charge density of the ion cloud outside the surface is

$$\rho_{w}(\mathbf{r}_{1}) = \sum_{j} \int d\mathbf{r}_{2} d\omega_{2} n_{j}(\mathbf{r}_{2}, \omega_{2}) \sigma_{j}(\mathbf{r}_{21}, \omega_{2}),$$

which can be regarded as the polarization charge density in the electrolyte due to the presence of the wall (a polarization due to all interactions, not only the electrostatic one, but the latter dominate far from the surface in the cases considered in this paper). The mean electrostatic potential  $\psi_w(\mathbf{r})$  is given by Eq. (6), as before.

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

$$\rho_{w}(\mathbf{r}_{1}) = \sum_{j} \int d\mathbf{r}_{2} d\omega_{2} n_{j}^{\mathrm{b}} e^{-\beta W_{j}(\mathbf{r}_{2},\omega_{2})} \sigma_{j}(\mathbf{r}_{21},\omega_{2}).$$
(34)

Sufficiently far away from the wall where the electrostatic field is weak,  $n_j(\mathbf{r})$  is close to  $n_j^b$  so  $W_j(\mathbf{r})$  is small and the exponential

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function can be expanded to linear order. We obtain when  $z_1 \rightarrow \infty$ 

$$\rho_{w}(\mathbf{r}_{1}) \sim \sum_{j} \int d\mathbf{r}_{2} d\omega_{2} n_{j}^{b} \left[ 1 - \beta W_{j}(\mathbf{r}_{2}, \omega_{2}) \right] \sigma_{j}(\mathbf{r}_{21}, \omega_{2})$$
$$= -\beta \sum_{j} \int d\mathbf{r}_{2} d\omega_{2} n_{j}^{b} W_{j}(\mathbf{r}_{2}, \omega_{2}) \sigma_{j}(\mathbf{r}_{21}, \omega_{2}) \qquad (35)$$

because  $\sum_j \int d\mathbf{r}_2 d\omega_2 n_j^b \sigma_j(\mathbf{r}_{21}, \omega_2) = \sum_j n_j^b q_j = 0$  by electroneutrality.

The deviation in density distribution from the bulk value far from the wall and hence the deviation of  $W_j$  from zero is due to the interactions of the particles with the electrostatic potential  $\psi_w(\mathbf{r})$ , which polarizes the bulk electrolyte there. As we have discussed in Section 2, the electrostatics is nonlocal. Since  $W_j$ accordingly is a linear functional of  $\psi_w$  when the latter is small, we can write (cf. Eq. (9))

$$W_j(\mathbf{r}_2, \boldsymbol{\omega}_2) = \int d\mathbf{r}_3 \boldsymbol{\psi}_w(\mathbf{r}_3) \boldsymbol{\rho}_j^*(\mathbf{r}_{23}, \boldsymbol{\omega}_2) \quad \text{(weak field)}$$
(36)

(the existence and uniqueness of  $\rho_j^*$  follow from Rietz' representation theorem in this case too). The entity  $\rho_j^*$  is the charge density of a *dressed ion* in analogy to the case of spherical ions discussed earlier (or a *dressed molecule* for an uncharged molecule) and we have  $\rho_j^*(\mathbf{r}, \boldsymbol{\omega}) = \sigma_j(\mathbf{r}, \boldsymbol{\omega}) + \rho_j^{dress}(\mathbf{r}, \boldsymbol{\omega})$ , where  $\rho_j^{dress}$  takes care of effects of ion-ion correlations in the interaction of the *j* particle with  $\psi_w$  when the latter is small (cf. Eq. (11)).

By inserting Eq. (36) into Eq. (35) we obtain when  $z_1 \rightarrow \infty$ 

$$\rho_{w}(\mathbf{r}_{1}) \sim -\beta \sum_{j} \int d\mathbf{r}_{3} \left[ \int d\mathbf{r}_{2} d\omega_{2} n_{j}^{b} \rho_{j}^{*}(\mathbf{r}_{23}, \omega_{2}) \sigma_{j}(\mathbf{r}_{21}, \omega_{2}) \right] \psi_{w}(\mathbf{r}_{3}),$$

where we have changed of the order of integration. Hence we have

$$\rho_{w}(\mathbf{r}_{1}) \sim \int d\mathbf{r}_{3} \psi_{w}(\mathbf{r}_{3}) \chi^{*}(r_{31}) \quad \text{when } z_{2} \to \infty, \qquad (37)$$

where  $\chi^*$  is defined as

$$\boldsymbol{\chi}^{*}(r_{31}) = -\beta \sum_{j} \int d\mathbf{r}_{2} d\boldsymbol{\omega}_{2} n_{j}^{\mathrm{b}} \boldsymbol{\rho}_{j}^{*}(\mathbf{r}_{23}, \boldsymbol{\omega}_{2}) \boldsymbol{\sigma}_{j}(\mathbf{r}_{21}, \boldsymbol{\omega}_{2}), \qquad (38)$$

i.e., the polarization response  $\chi^*$  function of the bulk liquid in the present case. The function  $\chi^*$  is spherically symmetric since an integration has been made over all orientations  $\omega_2$  in Eq. (38) and because of the fact that all functions in the expression refer to the properties of a bulk fluid. This definition of  $\chi^*$  constitutes the generalization of Eq. (13), see also Ref. 23.

#### 3.2 Polarization response, general case

The integral in the rhs of Eq. (37) (or Eq. (12) for the case of spherical ions) gives, as we have seen, the polarization charge density in the tail region away from the wall (at large *z*). This polarization arises due to the weak electrostatic potential  $\psi_w(\mathbf{r})$  there; the function  $\chi^*(r)$  is a linear response function for the bulk electrolyte. For smaller *z* the potential is not small, so the polarization charge density is not linearly related to  $\psi_w(\mathbf{r})$ . This means that this integral does not give the full charge density  $\rho_w(\mathbf{r})$ ; it only gives the *linear part* of the response to the electrostatic po-

tential. Let us consider the remainder of  $\rho_w(\mathbf{r})$  when the linear part has been removed, that is,

$$\rho_{w}(\mathbf{r}) - \int d\mathbf{r}' \psi_{w}(\mathbf{r}') \chi^{*}(|\mathbf{r} - \mathbf{r}'|) \equiv \rho_{w}^{\text{dress}}(\mathbf{r}), \qquad (39)$$

where we use the notation  $\rho_w^{dress}(\mathbf{r})$  for reasons to be explained later (it is, in fact, exactly the same kind of entity as the dress for the particles in the fluid). The charge density  $\rho_w^{dress}$  arises from the nonlinear part of the response to the electrostatic potential due to the wall and, in addition, from any nonelectrostatic effects that influence the particle density near the surface, like hard core exclusion and core-core correlations.

Next, we reformulate the Poisson equation (7) by subtracting the integral in Eq. (39) from both sides. The Poisson equation can thereby be written as

$$-\varepsilon_0 \nabla^2 \psi_w(\mathbf{r}) - \int d\mathbf{r}' \psi_w(\mathbf{r}') \chi^*(|\mathbf{r} - \mathbf{r}'|) = \sigma_w(\mathbf{r}) + \rho_w^{\text{dress}}(\mathbf{r}).$$
(40)

This equation has the solution

$$\psi_{w}(\mathbf{r}) = \int d\mathbf{r}' \left( \sigma_{w}(\mathbf{r}') + \rho_{w}^{dress}(\mathbf{r}') \right) \phi_{Coul}^{*}(|\mathbf{r} - \mathbf{r}'|), \qquad (41)$$

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

$$-\varepsilon_0 \nabla^2 \phi^*_{\text{Coul}}(r) - \int d\mathbf{r}' \phi^*_{\text{Coul}}(r') \boldsymbol{\chi}^*(|\mathbf{r} - \mathbf{r}'|) = \delta^{(3)}(r).$$
(42)

One can readily verify that  $\psi_w(\mathbf{r})$  from Eq. (41) satisfies Eq. (40) by direct insertion, whereby Eq. (42) is used to simplify the result. It follows from Eq. (41) that

$$\psi_{w}(\mathbf{r}) = \int d\mathbf{r}' \rho_{w}^{*}(\mathbf{r}') \phi_{\text{Coul}}^{*}(|\mathbf{r} - \mathbf{r}'|), \qquad (43)$$

where we have introduced the dressed wall charge density

$$\boldsymbol{\rho}_{w}^{*}(\mathbf{r}) = \boldsymbol{\sigma}_{w}(\mathbf{r}) + \boldsymbol{\rho}_{w}^{\text{dress}}(\mathbf{r}). \tag{44}$$

Note that Eq. (43) has exactly the same form as Coulomb's law. In this equation, the dressed wall charge density  $\sigma_w(\mathbf{r}) + \rho_w^{dress}(\mathbf{r})$  has the role of a source charge density when one uses the screened Coulomb potential  $\phi_{Coul}^*(r)$  to calculate the electrostatic potential  $\psi_w$ .<sup>||</sup> When one calculates the same potential  $\psi_w(\mathbf{r})$  using the unscreened Coulomb potential  $\phi_{Coul}(r)$  as in Eq. (6), the source charge density is  $\sigma_w(\mathbf{r}) + \rho_w(\mathbf{r}) \equiv \rho_w^{tot}(\mathbf{r})$ , i.e., the total charge density of the wall and its ion cloud.

In fact, the dressed ion charge density  $\rho_j^*(\mathbf{r}, \boldsymbol{\omega})$  that we introduced above, has the same role vis-á-vis the mean electrostatic potential  $\psi_j$  from an ion of species *j* in the bulk liquid phase. This potential is defined as

$$\psi_j(\mathbf{r},\boldsymbol{\omega}) = \int d\mathbf{r}' \boldsymbol{\rho}_j^{\text{tot}}(\mathbf{r}',\boldsymbol{\omega}) \phi_{\text{Coul}}(|\mathbf{r}-\mathbf{r}'|),$$

<sup>||</sup> Note that  $\rho_w^{dress}$  is nonzero inside the wall since  $\psi_w$  is nonzero there. This charge distribution in the wall is an entirely nominal charge distribution that expresses the excluded volume due to the wall in terms of a dress, see Ref. 26 for a discussion of this fact and for some mathematical aspects of this distribution.

where  $\rho_i^{\text{tot}} = \sigma_i + \rho_i$  and  $\rho_i$  is the charge density of the ion cloud that surrounds the ion. As shown in Ref. 23 we have

$$\psi_j(\mathbf{r},\boldsymbol{\omega}) = \int d\mathbf{r}' \rho_j^*(\mathbf{r}',\boldsymbol{\omega}) \phi_{\text{Coul}}^*(|\mathbf{r}-\mathbf{r}'|),$$

where the rhs shows that  $\psi_i$  can be calculated for all **r** by using the screened Coulomb potential and the charge density  $\rho_i^*$  of the dressed ion. This fact is one of the reasons for using the same terminology for walls and ions, i.e., "dressed wall" and "dressed ion."

In mathematical terms,  $\phi^*_{\text{Coul}}(r)$  as defined in Eq. (42) is a Green's function. Its physical role is to give the spatial propagation of the total electrostatic field (the so-called Maxwell field) including the contributions from polarization of the electrolyte to linear order. In the neighborhood of the surface, the nonlinear polarization must, however, also be included since the electrostatic field is strong there in general. This is done for  $\psi_w(r)$  via the contribution from  $\rho_w^{\text{dress}}$  in Eq. (41).

In the PB approximation, where  $\chi^*$  is given by Eq. (14),  $\phi^*_{Coul}$ equals

$$\phi_{\text{Coul}}^*(r) = \frac{e^{-\kappa_{\text{DH}}r}}{4\pi\epsilon_0 r}$$
 (PB).

In the general, exact case  $^{23}$   $\phi^*_{\rm Coul}(r)$  decays like

$$\phi_{\text{Coul}}^*(r) \sim A^* \frac{e^{-\kappa r}}{r}, \quad r \to \infty$$
 (45)

provided the electrostatic coupling is sufficiently weak [the coefficient  $A^*$  will be specified later, see Eq. (47)]. The decay parameter  $\kappa$  satisfies Eq. (20), as can be shown from Eq. (42) in a similar way as we derived Eq. (20) from Eq. (17).<sup>19</sup> In exactly the same manner as in Section 2.3 one can show that  $\kappa$  satisfies Eq. (28), that is,  $\kappa^2 = \frac{\beta}{\mathcal{E}_r^* \varepsilon_0} \sum_j n_j^{\mathrm{b}} q_j q_j^*,$ 

where

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

is the dressed ion charge in the current case. Remember that  $\mathcal{E}_r^* = \mathcal{E}_r^*(\kappa)$  depends on  $\kappa$ , so Eq. (46) is an equation for  $\kappa$ . This exact and amazingly simple equation is accordingly valid for the general case treated in this paper.

In Ref. 19 it is shown that the effective relative permittivity  $\mathcal{E}_r^*$  contains the same kind of contributions from the dipole moments of the ions as the dielectric constant  $\varepsilon_r$  does for polar liquids consisting of uncharged molecules. In addition, there are, as mentioned in Section 2.3, very important contributions from ion-ion correlations. In Ref. 19 it is also shown that in contrast to  $\varepsilon_r$ , which can be expressed solely in terms of dipolar features of the molecules in the pure polar liquid,  $\mathcal{E}_r^*$  for ionic liquids have contributions also from quadrupolar, octupolar and higher multipolar features of the constituent ions (and of polar molecules when present).

For a real solution  $\kappa$  of Eq. (46) (and Eq. (20)), the screened

Coulomb potential decays like\*\*

$$\phi_{\text{Coul}}^*(r) \sim \frac{e^{-\kappa r}}{4\pi \mathcal{E}_r^{\text{eff}} \varepsilon_0 r}, \quad r \to \infty,$$
(47)

where

$$\mathcal{E}_{r}^{\text{eff}} = 1 + \frac{1}{2\varepsilon_{0}} \int d\mathbf{r} r^{2} \left[ \frac{\kappa r \cosh(\kappa r) - \sinh(\kappa r)}{(\kappa r)^{3}} \right] \chi^{*}(r).$$
(48)

(Note that the square bracket in the integral remains finite when  $\kappa r \rightarrow 0.$ ) In Eq. (45) we accordingly have  $A^* = (4\pi \mathcal{E}_r^{\text{eff}} \varepsilon_0)^{-1}$ . Note that  $\mathcal{E}_r^{\text{eff}} = \mathcal{E}_r^{\text{eff}}(\kappa)$  is a function of  $\kappa$ . Both  $\mathcal{E}_r^{\text{eff}}$  and  $\mathcal{E}_r^*$  play roles as effective permittivities of the electrolyte and both are defined in terms of  $\chi^*(r)$ . Their relationship to each other and to the dielectric properties of the ionic liquid, in particular the static dielectric function, is examined in detail in Ref. 19.

When Eq. (46) (and Eq. (20)) has a solution  $\kappa$  that is complex, the parameter  $\mathcal{E}_r^{\mathrm{eff}} = \mathcal{E}_r^{\mathrm{eff}}(\kappa) = \mathcal{E}_r^{\mathrm{eff}}(\kappa_{\Re} \pm \mathrm{i}\kappa_{\Im})$  is also complex so we can write  $\mathcal{E}_r^{\text{eff}} = \mathsf{E}_r^{\text{eff}} \exp(\pm i\vartheta_{\mathsf{E}})$  where  $\mathsf{E}_r^{\text{eff}} = |\mathcal{E}_r^{\text{eff}}|$  and  $\vartheta_{\mathsf{E}}$  are real, and we have

$$\phi_{\text{Coul}}^{*}(r) \sim \frac{e^{-(\kappa_{\Re} + i\kappa_{\Im})r}}{4\pi \mathsf{E}_{r}^{\text{eff}} e^{\mathrm{i}\vartheta_{\mathsf{E}}} \varepsilon_{0}r} + \frac{e^{-(\kappa_{\Re} - i\kappa_{\Im})r}}{4\pi \mathsf{E}_{r}^{\text{eff}} e^{-\mathrm{i}\vartheta_{\mathsf{E}}} \varepsilon_{0}r}$$
$$= \frac{e^{-\kappa_{\Re}r} \cos(\kappa_{\Im}r + \vartheta_{\mathsf{E}})}{2\pi \mathsf{E}_{r}^{\text{eff}} \varepsilon_{0}r}$$
(49)

when  $r \to \infty$ .

(46)

In systems where some of the species are uncharged, like electrolyte solutions with polar solvent molecules,  $q_i$  is zero for these molecules, so the sum in Eq.(46) is hence only over the ionic species. Polar molecules participate in the dress of the ions, but they do not contribute directly to  $q_i^*$  since they are uncharged. They do, however, affect the value of  $q_i^*$  indirectly via correlations and they contribute directly to  $\mathcal{E}_r^*$ . From Eqs. (46) and (47) we see that  $\mathcal{E}_r^*$  and  $\mathcal{E}_r^{\text{eff}}$  in the general case take roles that the solvent's dielectric constant  $\varepsilon_r$  has for dilute electrolyte solutions. In the limit of infinite dilution we have  $\mathcal{E}_r^* \to \mathcal{E}_r$  and  $\mathcal{E}_r^{\text{eff}} \to \mathcal{E}_r$ . See Ref. 19 for a detailed discussion of these matters.

#### 3.3 Decay of the mean electrostatic potential from the wall

For simplicity, we start with the case of a wall with a uniformly smeared out surface density  $\sigma^{S}$  located at z = 0 and we initially assume that the wall is smooth so the nonelectrostatic ion-wall interaction does not depend on the x and y coordinates, i.e.,  $v_i^{sh} =$  $v_i^{
m sh}(z,\omega)$ . Thus, the charge densities  $ho_w$  and  $ho_w^*$  and the potential  $\psi_w$  depend only on z. We first treat the case when  $\kappa$  for the bulk electrolyte is real-valued. From Eqs. (43) and (47) it follows that

<sup>\*\*</sup> This decay behavior has been demonstrated in Ref. 23, where  $\phi^*_{\text{Coul}}(r)$  is denoted  $\phi^0(r)$ . For the case of spherical ions this was originally shown in Ref. 20, where  $\phi^*_{\text{Coul}}(r)\delta q$  is denoted  $\delta \Psi^{\text{av}}(r)$  and  $\delta q$  is an infinitesimally small point charge. The integral representation of  $\mathcal{E}_r^{\text{eff}}$  in Eq. (48) is given in Ref. 20.

the potential far from the surface decays like

$$\begin{split} \psi_w(z) &\sim \int d\mathbf{r}' \rho_w^*(z') \frac{e^{-\kappa |\mathbf{r}-\mathbf{r}'|}}{4\pi \mathcal{E}_r^{\text{eff}} \varepsilon_0 |\mathbf{r}-\mathbf{r}'|} \quad \text{when } z \to \infty \\ &= \frac{1}{4\pi \mathcal{E}_r^{\text{eff}} \varepsilon_0} \int dz' \rho_w^*(z') \int d\mathbf{s} \frac{e^{-\kappa [s^2 + (z-z')^2]^{1/2}}}{[s^2 + (z-z')^2]^{1/2}}, \end{split}$$

where  $\mathbf{s} = (x - x', y - y')$ ,  $s = |\mathbf{s}|$  and  $d\mathbf{s}$  can be replaced by  $2\pi s ds$ . The last integral can be done analytically, yielding

$$\psi_w(z) \sim \frac{1}{2\kappa \mathcal{E}_r^{\text{eff}} \varepsilon_0} \int dz' \rho_w^*(z') e^{-\kappa |z-z'|} \quad \text{when } z \to \infty.$$

In fact,  $\rho_w^*(z')$  is more short-ranged than  $\exp(-\kappa z')$ , <sup>26</sup> so we can take z' < z and in the limit  $z \to \infty$  we obtain

$$\Psi_w(z) \sim \frac{1}{2\kappa \mathcal{E}_r^{\text{eff}} \varepsilon_0} \left[ \int dz' \rho_w^*(z') e^{\kappa z'} \right] e^{-\kappa z},$$

where the integral is convergent. By defining an effective surface charge density

$$\sigma^{Seff} = \frac{1}{2} \int dz' \rho_w^*(z') e^{\kappa z'}$$
(50)

we can write this as

$$\Psi_{w}(z) \sim \frac{\sigma^{\mathcal{S}\text{eff}}}{\kappa \mathcal{E}_{r}^{\text{eff}} \varepsilon_{0}} e^{-\kappa z} \quad \text{when } z \to \infty.$$
(51)

This can be compared with the DH result for a surface with charge density  $\sigma^{S}$  in contact with an electrolyte in a solvent that has dielectric constant  $\varepsilon_r$ 

$$\psi_{w}(z) \sim \frac{\sigma^{S}}{\kappa_{\rm DH} \varepsilon_{r} \varepsilon_{0}} e^{-\kappa_{\rm DH} z} \quad (\rm DH),$$
(52)

which motivates the inclusion of the factor  $\frac{1}{2}$  in the definition of  $\sigma^{S \text{ eff}}$  (see also Ref. 26).

Let us now proceed to the general case where the internal charge distribution of the wall is  $\sigma_w(\mathbf{r})$  and the short-ranged interaction potential is  $v_j^{\text{sh}}(\mathbf{r}, \omega)$ . Then  $\rho_w(\mathbf{r})$ ,  $\rho_w^*(\mathbf{r})$  and  $\psi_w(\mathbf{r})$  depend also on *x* and *y*. It follows from Eq. (43) that

$$\psi_{w}(\mathbf{r}) \sim \int d\mathbf{r}' \rho_{w}^{*}(\mathbf{r}') \frac{e^{-\kappa |\mathbf{r} - \mathbf{r}'|}}{4\pi \mathcal{E}_{r}^{\text{eff}} \varepsilon_{0} |\mathbf{r} - \mathbf{r}'|} \quad \text{when } z \to \infty.$$
 (53)

As shown in Appendix A, the *x* and *y* dependences of  $\psi_w(\mathbf{r})$  vanish when  $z \to \infty$  more quickly than the *z* dependence, which still goes like  $\exp(-\kappa z)$ . Thus,  $\psi_w(\mathbf{r})$  ultimately depends only on *z* for large *z*. This means that the potential still decays like in Eq. (51), i.e.,

$$\psi_w(\mathbf{r}) \sim \frac{\sigma^{\mathcal{S}\text{eff}}}{\kappa \mathcal{E}_r^{\text{eff}} \varepsilon_0} e^{-\kappa z} \quad \text{when } z \to \infty,$$
(54)

where, as shown in Appendix A, the effective surface charge density in this case is given by

$$\sigma^{Seff} = \frac{1}{2\mathcal{A}} \int d\mathbf{r}' \rho_{w}^{*}(\mathbf{r}') e^{\kappa z'}, \qquad (55)$$

with  $\mathcal{A}$  being the area of the surface ( $\sigma^{Seff}$  is in principle evaluated in the limit of an infinitely large surface, see Appendix A).

#### 3.4 Potential of mean force acting on ions outside a wall

The potential of mean force acting on an ion (or other particle) of species *j* is given by Eq. (36) in the tail region in the limit of large *z*. By inserting our result (54) for  $\psi_w$  and utilizing the fact that this potential depends only on *z* for large *z* we obtain

$$W_{j}(\mathbf{r}_{1},\boldsymbol{\omega}_{1}) \sim \frac{\sigma^{\mathcal{S}\text{eff}}}{\kappa \mathcal{E}_{r}^{\text{eff}} \boldsymbol{\varepsilon}_{0}} \int d\mathbf{r}_{2} e^{-\kappa z_{2}} \rho_{j}^{*}(\mathbf{r}_{12},\boldsymbol{\omega}_{1}) \quad \text{when } z_{1} \to \infty,$$
$$= \frac{\sigma^{\mathcal{S}\text{eff}} e^{-\kappa z_{1}}}{\kappa \mathcal{E}_{r}^{\text{eff}} \boldsymbol{\varepsilon}_{0}} \int d\mathbf{r}_{2} e^{-\kappa (z_{2}-z_{1})} \rho_{j}^{*}(\mathbf{r}_{2}-\mathbf{r}_{1},\boldsymbol{\omega}_{1}).$$

By setting  $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$  and keeping  $\mathbf{r}_1$  constant during the integration so  $d\mathbf{r}_2 = d(\mathbf{r}_2 - \mathbf{r}_1)$ , we can write the integral as

$$\int d\mathbf{r} \, e^{-\kappa z} \rho_j^*(\mathbf{r}, \omega_1) = \int d\mathbf{r} \, e^{-\kappa \mathbf{r} \cdot \hat{\mathbf{z}}_1} \rho_j^*(\mathbf{r}, \omega_1) = \mathsf{Q}_j^{\text{eff}}(-\hat{\mathbf{z}}_1, \omega_1)$$

where  $\hat{\mathbf{z}}_1$  is the normal to the surface (which defines the *z* direction) and  $Q_i^{\text{eff}}$  is defined from

$$Q_{j}^{\text{eff}}(\hat{\mathbf{r}}',\boldsymbol{\omega}) = \int d\mathbf{r} \, e^{\mathbf{k}\mathbf{r}\cdot\hat{\mathbf{r}}'} \rho_{j}^{*}(\mathbf{r},\boldsymbol{\omega})$$
(56)

with  $\hat{\textbf{r}}'=-\hat{\textbf{z}}_{1}$  in our case. Thus we have

$$W_j(\mathbf{r}_1, \boldsymbol{\omega}_1) \sim \sigma^{\mathcal{S}\text{eff}} \mathsf{Q}_j^{\text{eff}}(-\hat{\mathbf{z}}_1, \boldsymbol{\omega}_1) \frac{e^{-\kappa_{z_1}}}{\kappa \mathcal{E}_r^{\text{eff}} \boldsymbol{\varepsilon}_0} \quad \text{when } z_1 \to \infty, \quad (57)$$

which means that the magnitude of the interaction is proportional to the product of the effective surface charge density of the wall and an effective interaction parameter  $Q_j^{\text{eff}}$  of the ion. The latter is the entity that gives the magnitude of the screened electrostatic interactions between ions (or molecules) in bulk electrolytes as shown in Ref. 24 (in this reference the entity  $Q^{\text{eff}}$  is denoted  $a_0$ ). The leading term for the potential of mean force  $w_{ij}$  between two ions of species *i* and *j* when the separation  $r_{12} \rightarrow \infty$  is given by<sup>24</sup>

$$w_{ij}(\mathbf{r}_{12},\boldsymbol{\omega}_1,\boldsymbol{\omega}_2) \sim \mathsf{Q}_i^{\mathrm{eff}}(\hat{\mathbf{r}}_{12},\boldsymbol{\omega}_1) \mathsf{Q}_j^{\mathrm{eff}}(-\hat{\mathbf{r}}_{12},\boldsymbol{\omega}_2) \frac{e^{-\kappa r_{12}}}{4\pi \mathcal{E}_r^{\mathrm{eff}} \varepsilon_0 r_{12}}, \quad (58)$$

where the interaction parameter  $Q_l^{\text{eff}}$ , with l = i or j, depends on the orientation of each ion and the direction of the vector  $\mathbf{r}_{12}$  that joins the centers of the two ions (i.e., for a given orientations  $\omega_1$ and  $\omega_2$ , which are defined relative to the laboratory frame,  $Q_l^{\text{eff}}$ depends on the direction of  $\mathbf{r}_{12}$ ). Note that for  $Q_j^{\text{eff}}$  in Eq. (57) the vector  $-\hat{\mathbf{z}}_1$  points towards the surface, which is in complete analogy to the vector  $-\hat{\mathbf{r}}_{12}$  in  $Q_j^{\text{eff}}$  in Eq. (58), which points towards the *i* ion.

The screened electrostatic part  $w_{ij}^{\text{el}}$  of the potential of mean force  $w_{ij}$  is in the general case given by<sup>††</sup>

$$w_{ij}^{\text{el}}(\mathbf{r}_{12},\omega_1,\omega_2) = \int d\mathbf{r}_3 d\mathbf{r}_4 \rho_i^*(\mathbf{r}_{13},\omega_1) \phi_{\text{Coul}}^*(r_{34}) \rho_j^*(\mathbf{r}_{24},\omega_2)$$
(59)

for all distances between the ions. This has the same form as

<sup>††</sup> In Refs. 23,24 it is shown that  $w_{ij}^{el}$ , as defined in Eq. (59), is a term in  $w_{ij}$  that contributes for all  $\mathbf{r}_{12}$ . Despite that  $w_{ij}^{el}$  contains interactions with dressed ion charge distributions, it is *not* a weak field expression that is restricted to the asymptotic regime at large distances. The complete expression for  $w_{ij}$  is given in Eqs. (81) and (82) of Ref. 23.

the electrostatic energy calculated using Coulomb's law, but with the screened Coulomb potential acting between the dressed ion charge distributions of the two ions. When the electrostatic interactions dominate for large  $r_{12}$  (as in the cases considered in the current work) we have  $w_{ij}(\mathbf{r}_{12}, \omega_1, \omega_2) \sim w_{ij}^{\text{el}}(\mathbf{r}_{12}, \omega_1, \omega_2)$  when  $r_{12} \rightarrow \infty$ . Eq. (58) gives the leading term of  $w_{ij}^{\text{el}}$  for large  $r_{12}$  when  $\kappa$  is real and therefore also the leading term of  $w_{ij}$ . Likewise, for the wall-ion potential of mean force  $W_j$ , the screened electrostatic part  $W_j^{\text{el}}$  is in general given by

$$W_j^{\text{el}}(\mathbf{r}_1, \boldsymbol{\omega}_1) = \int d\mathbf{r}_3 \boldsymbol{\psi}_w(\mathbf{r}_3) \boldsymbol{\rho}_j^*(\mathbf{r}_{13}, \boldsymbol{\omega}_1)$$
(60)

$$= \int d\mathbf{r}_2 d\mathbf{r}_3 \boldsymbol{\rho}_w^*(\mathbf{r}_2) \boldsymbol{\phi}_{\text{Coul}}^*(r_{23}) \boldsymbol{\rho}_j^*(\mathbf{r}_{13}, \boldsymbol{\omega}_1) \quad (61)$$

which is defined for all  $\mathbf{r}_1$ . Note that the first equality, Eq. (60), is the same as Eq. (36) but in contrast to the latter, Eq. (60) is *not* limited to weak fields (as found for large distances from the wall) but is valid in general. The last equality, Eq. (61), is obtained by inserting Eq. (43), which is also of general validity. In the cases considered in this work  $W_j(\mathbf{r}_1, \boldsymbol{\omega}_1) \sim W_j^{\rm el}(\mathbf{r}_1, \boldsymbol{\omega}_1)$  when  $z_1 \rightarrow \infty$  and Eq. (57) gives the leading term when  $\kappa$  is real. For the oscillatory case when  $\kappa$  is complex-valued, the leading term corresponding to Eq. (57) can be obtained by adding two such terms (complex conjugates) as has been described earlier.

#### 3.5 Surface forces

Let us now treat interactions between two planar surfaces in contact with an electrolyte. Consider two parallel walls I and II that have an electrolyte in the slit between the surfaces. This electrolyte is in equilibrium with a bulk electrolyte with density  $n_i^{\rm b}$  for each species *i* present. Wall I is infinitely large laterally, while wall II initially has a finite, albeit very large, surface area  $\mathcal{A}_{\rm II}$ . We will later let  $\mathcal{A}_{\rm II} \rightarrow \infty$  in order to obtain the interaction per unit area between two infinite surfaces at large surface separations. Since wall II is very large, we will neglect the edge effects of the surface on the interaction. These effects vanish in the interaction per unit area when  $\mathcal{A}_{\rm II} \rightarrow \infty$ . Furthermore, the walls are very thick.

When wall II is infinitely far from wall I, the electrostatic potential from the latter decays like (from Eq. (54))

$$\psi_{\mathrm{I}}(\mathbf{r}) \sim rac{\sigma_{\mathrm{I}}^{\mathcal{S}\mathrm{eff}}}{\kappa \mathcal{E}_{r}^{\mathrm{eff}} \varepsilon_{0}} e^{-\kappa z} \quad \mathrm{when} \; z 
ightarrow \infty,$$

where  $\sigma_{I}^{Seff}$  is defined as in Eq. (55). Let wall II approach wall I. The distance between the surfaces is *L* as measured between the origin placed at surface I and a similarly placed origin at surface II (i.e., the origin of a local coordinate system for II with *z* axis in the opposite direction compared to that of wall I). Still, wall I defines the origin of our (global) coordinate system (*x*, *y*, *z*).

Since our result in Eq. (57) is of general validity for a particle of any size, shape and charge distribution placed at coordinate z, it is also valid for the potential of mean force  $W_{\text{II}}$  acting on wall II in the presence of wall I. We have

$$\mathsf{Q}_{\mathrm{II}}^{\mathrm{eff}}(-\hat{\mathbf{z}}_{1},\omega) = \mathsf{Q}_{\mathrm{II}}^{\mathrm{eff}}(\hat{\mathbf{z}}_{\mathrm{II}},\omega) = \int d\mathbf{r}' e^{\kappa \mathbf{r}'\cdot\hat{\mathbf{z}}_{\mathrm{II}}} \rho_{\mathrm{II}}^{*}(\mathbf{r}',\omega),$$

where  $\hat{\mathbf{z}}_{\text{II}}$  is the local normal of surface II,  $\rho_{\text{II}}^*$  is the dressed charge density of wall II and the last equality follows from Eq. (56). The orientation  $\omega$ , which is written explicitly here, is also implicit in  $\rho_{\text{II}}^*$  for the wall. From the definition (55) follows that  $\int d\mathbf{r}' \exp(\kappa \mathbf{r}' \cdot \hat{\mathbf{z}}_{\text{II}}) \rho_{\text{II}}^*(\mathbf{r}', \omega) = 2\mathcal{A}_{\text{II}} \sigma_{\text{II}}^{Seff}$  since  $\mathbf{r}' \cdot \hat{\mathbf{z}}_{\text{II}} = z'$  in the local coordinate system for II (we select this local coordinate system for  $\mathbf{r}'$  in the integral; this is in congruence with the choice of coordinate system in Eq. (55) when applied to wall I). Thus, by using this result and defining the interaction free energy (potential of

$$\mathscr{W}_{I,II}(L) \sim \sigma_{I}^{Seff} \sigma_{II}^{Seff} \frac{2e^{-\kappa L}}{\kappa \mathcal{E}_{c}^{eff} \varepsilon_{0}} \quad \text{when } L \to \infty,$$
 (62)

(note that  $z_1$ , which is the distance from wall I in Eq. (57), has here been replaced by *L*). Compare this with the Debye-Hückel result

mean force) per unit area for the interaction between I and II as

 $\mathcal{W}_{I,II} = W_{II}/\mathcal{A}_{II}$ , we obtain from Eq. (57) in the limit of  $\mathcal{A}_{II} \to \infty$ 

$$\mathscr{W}_{\mathrm{I,II}}(L) \sim \sigma_{\mathrm{I}}^{\mathcal{S}} \sigma_{\mathrm{II}}^{\mathcal{S}} \frac{2e^{-\kappa_{\mathrm{DH}}L}}{\kappa_{\mathrm{DH}} \epsilon_{r} \epsilon_{0}} \quad \text{(DH)}$$

for the interaction between two surfaces with surface charge densities  $\sigma_I^{\cal S}$  and  $\sigma_I^{\cal S}.$ 

When  $\kappa$  is complex valued, with  $\kappa_{\Re} \pm i\kappa_{\Im}$  being the two complex conjugate solutions to Eq. (20), we have the two contributions to the mean electrostatic potential

$$\begin{split} \psi_{\mathrm{I}}(\mathbf{r}) &\sim \quad \frac{\sigma_{\mathrm{I}}^{\mathcal{S}\mathrm{eff}}}{(\kappa_{\mathfrak{R}} + \mathrm{i}\kappa_{\mathfrak{I}})\mathcal{E}_{r}^{\mathrm{eff}}\varepsilon_{0}}e^{-(\kappa_{\mathfrak{R}} + \mathrm{i}\kappa_{\mathfrak{I}})z} \\ &+ \quad \frac{\underline{\sigma}_{\mathrm{I}}^{\mathcal{S}\mathrm{eff}}}{(\kappa_{\mathfrak{R}} - \mathrm{i}\kappa_{\mathfrak{I}})\underline{\mathcal{E}}_{r}^{\mathrm{eff}}\varepsilon_{0}}e^{-\kappa(\kappa_{\mathfrak{R}} - \mathrm{i}\kappa_{\mathfrak{I}})} \quad \mathrm{when} \ z \to \infty, \ (63) \end{split}$$

where underline means complex conjugate,

$$\sigma_{\mathrm{I}}^{\mathcal{S}\mathrm{eff}} = \frac{1}{2\mathcal{A}} \int d\mathbf{r}' \rho_{\mathrm{I}}^{*}(\mathbf{r}') e^{(\kappa_{\mathfrak{R}} + \mathrm{i}\kappa_{\mathfrak{I}})z'} = |\sigma_{\mathrm{I}}^{\mathcal{S}\mathrm{eff}}| e^{-\mathrm{i}\gamma_{\mathrm{I}}}$$

with a real-valued  $\gamma_{\rm I}$ , and where  $\mathcal{E}_r^{\rm eff} = \mathsf{E}_r^{\rm eff} \exp(\mathrm{i}\vartheta_{\mathsf{E}})$  is given by Eq. (48) evaluated at  $\kappa = \kappa_{\Re} + \mathrm{i}\kappa_3$ . Writing  $\kappa_{\Re} + \mathrm{i}\kappa_3 = \mathrm{K}\exp(\mathrm{i}\vartheta_{\mathsf{K}})$  with real K and  $\vartheta_{\mathsf{K}}$ , we obtain from Eq. (63) the oscillatory decay

$$\psi_{\rm I}(\mathbf{r}) \sim \frac{2|\sigma_{\rm I}^{S\rm eff}|e^{-\kappa_{\Re z}}}{{\sf K}{\sf E}_r^{\rm eff}\varepsilon_0}\cos(\kappa_{\Im z} + \vartheta_{\sf E\sf K} + \gamma_{\rm I}) \quad \text{when } z \to \infty, \quad (64)$$

where  $\vartheta_{\mathsf{EK}} = \vartheta_{\mathsf{E}} + \vartheta_{\mathsf{K}}$ . For the interaction free energy we likewise obtain when  $L \to \infty$ 

$$\mathscr{W}_{\mathrm{I},\mathrm{II}}(L) \sim \frac{4|\sigma_{\mathrm{I}}^{\mathcal{S}\mathrm{eff}}\sigma_{\mathrm{II}}^{\mathcal{S}\mathrm{eff}}|e^{-\kappa_{\Re}L}}{\mathsf{K}\mathsf{E}_{r}^{\mathrm{eff}}\varepsilon_{0}}\cos(\kappa_{\Im}L + \vartheta_{\mathsf{EK}} + \gamma_{\mathrm{I}} + \gamma_{\mathrm{II}}) \qquad (65)$$

and we see that the surfaces contributes with phase shifts  $\gamma_I$  and  $\gamma_{II}$  apart from the magnitudes  $|\sigma_I^{Seff}|$  and  $|\sigma_{II}^{Seff}|$ .

Thus, Eqs. (62) and (65) gives the decay of the interaction free energy  $\mathscr{W}_{I,II}(L)$  per unit area between two planar surfaces for the two cases of plain exponential decay (real-valued  $\kappa$ ) and exponentially damped, oscillatory decay (complex-valued  $\kappa$ ), respectively. The surface force  $\mathscr{F}_{I,II}$  per unit area between the two walls is  $\mathscr{F}_{I,II} = -d\mathscr{W}_{I,II}(L)/dL$ .

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#### 4 Conclusions

The free energy of electrostatic interaction per unit area,  $\mathcal{W}_{I,II}$ , between two walls I and II immersed in a bulk electrolyte decays when the separation increases in either an damped oscillatory or a monotonic manner. Both behaviors can appear in ionic liquids and other electrolytes. At sufficiently large surface separations the interaction free energy is proportional to the product of the effective surface charge densities,  $\sigma_{I}^{Seff}$  and  $\sigma_{I}^{Seff}$ , of the walls

$$\mathscr{W}_{I,II}(L) \sim \sigma_{I}^{Seff} \sigma_{II}^{Seff} 2C_1 e^{-\kappa L} \quad \text{when } L \to \infty$$

for the monotonic case and

$$\begin{aligned} \mathscr{W}_{I,\mathrm{II}}(L) &\sim & |\sigma_{\mathrm{I}}^{\mathcal{S}\mathrm{eff}}\sigma_{\mathrm{II}}^{\mathcal{S}\mathrm{eff}}|2C_{2}e^{-\kappa_{\mathfrak{R}}L} \\ &\times & \cos(\kappa_{\mathfrak{R}}L + \vartheta_{\mathsf{EK}} + \eta_{\mathsf{I}} + \eta_{\mathrm{II}}) \quad \mathrm{when} \ L \to \infty \end{aligned}$$

for the oscillatory case, where  $\gamma_1$  and  $\gamma_{II}$  are the phase shifts of the respective surface (Section 3.5).  $C_1$ ,  $C_2$  and  $\vartheta_{EK}$  are constants (specified below) that are determined by the bulk electrolyte. The interaction has the same kind of decay, the same decay length,  $1/\kappa$  or  $1/\kappa_{\Re}$  respectively, and wave length,  $2\pi/\kappa_3$ , as the screened Coulomb potential of the bulk. The walls can have a wide range of internal structures; they can have an arbitrary internal charge distribution and any non-electrostatic ion-wall interactions, provided the latter are sufficiently short-ranged. The electrolyte can consist of ions and other molecules of any shapes and any internal charge distributions. Their nonelectrostatic interactions are assumed to be short-ranged too.

The same decay behavior (with the same decay parameters  $\kappa$  or  $\kappa_{\Re}$  and  $\kappa_3$ ) applies for the electrostatic interactions between all particles in the system (ions, molecules and other particles), between the particles and a surface, and between two surfaces provided the separations are sufficiently large. However, specific properties of individual surfaces lie behind possible occurrences of some oscillations at small distances in cases when the ultimate decay is plain exponential. Such oscillations can exist for one surface in contact with the electrolyte but not necessarily for another surface in contact with the same electrolyte. What distance is sufficient for the ultimate decay to take over is system-dependent; the distance need not be very large<sup>15,32</sup> (it can be as short as a couple of ionic diameters in some cases).

An important conclusion of the current work is that the experimentally observed, long-ranged monotonic exponential decay  $^{9-11}$  for surface forces in ionic liquids *do not contradict theory for diffuse double layer interactions*, provided the latter is correctly applied to dense electrolytes. When nonlocal electrostatics is appropriately treated and the correct expression for the decay parameter  $\kappa$  is used (equation (66) below), the occurrences of both plain exponential and exponentially damped, oscillatory decay are accommodated in the theoretically predicted behaviors of ionic liquids and other very dense electrolytes. Furthermore, likely conditions for the appearance of the plain exponential decay instead of the oscillatory one are related to various possible reasons for transient associations of anions and cations. Since the ions are closely together in ionic liquids and since each ion

is surrounded by several ions of opposite sign, but also by ions of the same sign, the term "association" should hereby in general be interpreted in terms of how the ions correlate to each other rather than in terms of well defined long-lived complexes. This does not exclude, however, that entities like ion pairs are transiently formed in particular cases. An important point is that such pairing is not necessary for long-ranged monotonic exponential decay to occur.

The nonlocal nature of electrostatics in an ionic liquid or other electrolyte is due to correlations between the ions (and other molecules when present). The nonlocality can be expressed in terms of a polarization response function  $\chi^*(r)$  in linear response theory (Sections 2.1 and 3.1); this function is closely related to the electric susceptibility of the bulk electrolyte.<sup>‡‡</sup> The screening parameter  $\kappa$  satisfies the equation

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

This equation can be written in terms of an effective relative permittivity  $\mathcal{E}_r^*(\kappa)$  and renormalized charges of the ions  $q_j^*$  (the dressed ion charge which is the integral of the charge distribution  $\rho_i^*$ ) in the following manner (Sections 2.3 and 3.2)

$$\kappa^2 = \frac{\beta}{\mathcal{E}_r^*(\kappa)\varepsilon_0} \sum_j n_j^{\rm b} q_j q_j^*. \tag{66}$$

These two equations for  $\kappa$  are equivalent. Real-valued solutions  $\kappa$  give plain exponential decay and complex-valued solutions  $\kappa = \kappa_{\Re} + i\kappa_{\Im}$  give exponentially damped, oscillatory decay.

Long-ranged plain exponential decay in ionic liquids (associated with a real solution  $\kappa$  with a small value), can, for example, occur when the renormalized charges  $q_i^*$  for all species are small. In cases where  $\mathcal{E}_r^*(0)$  is large the values of  $q_i^*$  do not need to be very small for such a solution to exist. Small  $q_i^*$  can appear when there is a large degree of association of anions and cations, for instance ion pairs, but other kinds of transient associations are also possible, for example caused by many-body ion-ion correlations or by specific anion-cation attractions in addition to the plain electrostatic ones. A large  $\mathcal{E}_r^*(0)$  corresponds to large dipole-dipole contributions<sup>19</sup> from correlations both involving permanent dipoles of the ions and transient association "complexes." Most significantly, the values of  $\mathcal{E}_r^*(\kappa)$  for  $\kappa \neq 0$  contains contributions from quadrupolar and higher multipolar features of the ions and of association complexes. Thus, not only the dipolar features are important in general. These and other properties of  $\mathcal{E}_r^*$  are extensively discussed in a separate paper, Ref. 19, where also the relationships between  $\kappa$ ,  $\mathcal{E}_r^*$ ,  $\mathcal{E}_r^{\text{eff}}$  and the static dielectric function of the ionic liquid are treated in detail.

For a single wall immersed in an ionic liquid or other electrolyte, the average electrostatic potential  $\psi_w(\mathbf{r})$  from the wall depends in general on all three coordinates *x*, *y* and *z*, where

 $<sup>\</sup>ddagger$  The electric susceptibility, which relates the polarization field to the total electrostatic field (the Maxwell field), is the Fourier transform  $\tilde{\chi}(k)$  of  $\chi(r_{12}) = \int d\mathbf{r}_3 \chi^*(r_{13}) \phi_{\text{Coul}}(r_{32})$  and the static dielectric function of the bulk electrolyte is  $\tilde{\epsilon}(k) = 1 - \tilde{\chi}(k)$ .

z is the distance from the wall surface. At increasing distance from the surface, the x and y dependences of the potential do, however, decay quite quickly and eventually only the z dependence remain in practice (Section 3.3). Therefore, for the case of monotonic exponential decay of the potential, the values of  $\psi_w$  for large z can be the same as the values of the potential from a perfectly smooth surface with some uniformly smeared out surface charge density  $\sigma^{S}$  and without internal structure. The same applies to the surface interaction  $\mathcal{W}_{LII}$  for large surface separations described above. The value of  $\sigma^{S}$  for the surface with uniform surface charge density is, however, not the same as the average charge density per unit area of the original wall with internal structure. By definition, both surfaces - the original one and the smooth one - do have the same effective surface charge density  $\sigma^{Seff}$ , which is defined from the magnitude of the potential in the asymptotic decay region at large z,

$$\Psi_w(\mathbf{r}) \sim \sigma^{Seff} C_1 e^{-\kappa z}$$
 when  $z \to \infty$ ,

where the entities  $C_1 = 1/(\mathcal{E}_r^{\text{eff}} \varepsilon_0 \kappa)$  and  $\kappa$  are properties of the bulk electrolyte alone. For the case of exponentially damped, oscillatory decay, the wall gives rise to a phase shift  $\gamma$  of the potential (Section 3.5)

$$\psi_{w}(\mathbf{r}) \sim |\sigma^{Seff}| C_2 e^{-\kappa_{\Re} z} \cos(\kappa_{\Im} z + \vartheta_{\mathsf{EK}} + \gamma) \quad \text{when } z \to \infty,$$

where all entities except  $|\sigma^{Seff}|$  and  $\gamma$  are properties of the bulk electrolyte alone, i.e., the entities  $C_2 = 2/(|\mathcal{E}_r^{eff}|\varepsilon_0|\kappa|)$ ,  $\kappa_{\Re}$ ,  $\kappa_{\Im}$  and  $\vartheta_{\mathsf{EK}} = \vartheta_{\mathsf{E}} + \vartheta_{\mathsf{K}}$  (here,  $\kappa = \kappa_{\Re} + i\kappa_{\Im} = |\kappa|\exp(i\vartheta_{\mathsf{K}})$  and  $\mathcal{E}_r^{eff} = |\mathcal{E}_r^{eff}|\exp(i\vartheta_{\mathsf{E}})$ ). The  $\gamma$  value is in general different for different surfaces even if they have the same value of  $|\sigma^{Seff}|$ .

The effective surface charge density of a wall with a large surface area  $\mathcal{A}$  is expressed in a straightforward manner in terms of the charge distribution  $\rho_w^*(\mathbf{r})$  of the so-called *dressed wall* (introduced in Section 3.2) according to

$$\sigma^{\mathcal{S}\text{eff}} = \frac{1}{2\mathcal{A}} \int d\mathbf{r} \rho_w^*(\mathbf{r}) e^{\kappa z}$$

(in principle in the limit of infinite  $\mathcal{A}$ ). A dressed wall can be characterized as follows. The average electrostatic potential  $\psi_w(\mathbf{r})$  is given for *all*  $\mathbf{r}$  by Coulomb's law either (i) in terms of the screened Coulomb potential  $\phi_{\text{Coul}}^*(r)$  of the bulk electrolyte and the dressed wall charge distribution  $\rho_w^*(\mathbf{r})$ 

$$\boldsymbol{\psi}_{w}(\mathbf{r}_{1}) = \int d\mathbf{r}_{2} \boldsymbol{\rho}_{w}^{*}(\mathbf{r}_{2}) \boldsymbol{\phi}_{\text{Coul}}^{*}(r_{21}),$$

or, equivalently, (ii) in terms of the usual (unscreened) Coulomb potential  $\phi_{\text{Coul}}(r)$  and the total charge distribution  $\rho_w^{\text{tot}}(\mathbf{r})$  due to the wall [i.e., the sum of its internal charge distribution  $\sigma_w$  and the charge density  $\rho_w$  of its ion cloud]

$$\Psi_w(\mathbf{r}_1) = \int d\mathbf{r}_2 \rho_w^{\text{tot}}(\mathbf{r}_2) \phi_{\text{Coul}}(r_{21}) + \text{ const.}$$

(const. is selected so  $\psi_w$  is zero in the bulk liquid at  $z_1 \to \infty$ ). The equivalence follows from the fact that the charge density  $\rho_w^*$  is equal to  $\rho_w^{\text{tot}}$  minus the linear part of the polarization response of the electrolyte due to  $\psi_w$ , as shown in Section 3.2.

The free energy of interaction (potential of mean force)  $W_j$  between a single wall and a *j* ion located at  $\mathbf{r}_1$  and with orientation  $\omega_1$  decays as

$$W_j(\mathbf{r}_1, \boldsymbol{\omega}_1) \sim \int d\mathbf{r}_2 \psi_w(\mathbf{r}_2) \boldsymbol{\rho}_j^*(\mathbf{r}_{12}, \boldsymbol{\omega}_1) \quad \text{when } z_1 \to \infty,$$

where  $\rho_j^*$  is the charge density of a dressed ion of species *j*. This holds provided the screened electrostatic interaction dominates for large distances. In the general case, the right hand side gives the *screened electrostatic part* of  $W_j$  for all  $\mathbf{r}_1$  outside the surface – not only for large  $z_1$ . For a bare ion the electrostatic interaction energy would be  $\int d\mathbf{r}_2 \psi_w(\mathbf{r}_2) \sigma_j(\mathbf{r}_{12}, \omega_1)$ , where  $\sigma_j$  is the internal (bare) charge density of the ion. The appearance of  $\rho_j^*$  instead of  $\sigma_j^*$  in the formula for  $W_j$  expresses the nonlocal nature of the electrostatic interactions in the ionic liquid, as explained in Section 3.1 (see also Section 2.1).

For large separations,  $W_j$  is proportional to the product of the effective surface charge density of the wall and an orientation dependent factor,  $Q_j^{\text{eff}}$ , from the ion (the latter originates from the dressed ion charge density of the *j* ion, as shown in Section 3.4). For the oscillatory case there also appears a phase shift from the wall and an orientation dependent phase shift from the ion (the latter contained in  $Q_i^{\text{eff}}$ ).

#### Appendix

#### A Decay of screened electrostatic potential from a planar surface

In this appendix we shall investigate long-range decay of the screened electrostatic potential  $\psi_w$  from a surface with an internal charge distribution  $\sigma_w(\mathbf{r})$  that depends on all coordinates, including the lateral coordinates *x* and *y*. The surface has infinite lateral extent, but in some arguments below we consider a finite surface of area  $\mathcal{A}$  in the limit  $\mathcal{A} \to \infty$  to obtain the infinitely large case. Initially we assume that the decay parameter  $\kappa$  is real. We will use Eq. (53) to determine the potential from the dressed surface charge distribution  $\rho_w^*(\mathbf{r}) = \sigma_w(\mathbf{r}) + \rho_w^{dress}(\mathbf{r})$ , but we will start with the contribution from  $\sigma_w$  which we denote  $\psi_w^{\sigma}$ . It decays as

$$\psi_{w}^{\sigma}(\mathbf{r}) \sim \int d\mathbf{r}' \sigma_{w}(\mathbf{r}') \frac{e^{-\kappa |\mathbf{r}-\mathbf{r}'|}}{4\pi \mathcal{E}_{r}^{\text{eff}} \varepsilon_{0} |\mathbf{r}-\mathbf{r}'|} \quad \text{when } z \to \infty.$$
(67)

Since the rhs is a convolution it can be written in Fourier space as a product and we obtain

$$\psi_{w}^{\sigma}(\mathbf{r}) \sim \frac{1}{\mathcal{E}_{r}^{\text{eff}} \varepsilon_{0}(2\pi)^{3}} \int d\mathbf{k} \frac{\widetilde{\sigma}_{w}(\mathbf{k})}{\kappa^{2} + k^{2}} e^{i\mathbf{k}\cdot\mathbf{r}} \quad \text{when } z \to \infty, \qquad (68)$$

where  $1/(\kappa^2 + k^2)$  is the Fourier transform (FT) of  $\exp(-\kappa r)/(4\pi r)$ ,  $\tilde{\sigma}_w$  is the FT of  $\sigma_w$ , and we have made an inverse FT.

Consider first the special case when  $\sigma_w(\mathbf{r}) = \delta(z)\sigma^{\mathcal{S}}(x,y) = \delta(z)\sigma^{\mathcal{S}}(\mathbf{r}_{xy})$  where  $\mathbf{r}_{xy} = (x,y)$ , that is, a nonuniform surface charge density located at z = 0. Then  $\tilde{\sigma}_w(\mathbf{k}) = \overline{\sigma}^{\mathcal{S}}(\mathbf{k}_{xy})$ , where  $\mathbf{k}_{xy} = (k_x, k_y)$  and  $\overline{\sigma}^{\mathcal{S}}(\mathbf{k}_{xy})$  is the two-dimensional FT of  $\sigma^{\mathcal{S}}(\mathbf{r}_{xy})$ . We will split  $\sigma^{\mathcal{S}}$  in two parts

$$\sigma^{\mathcal{S}}(\mathbf{r}_{xy}) = \sigma^{\mathcal{S}}_{Av} + \sigma^{\mathcal{S}}_{R}(\mathbf{r}_{xy}), \tag{69}$$

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(70)

 $\overline{\sigma}_{R}^{S}(\mathbf{0}) = 0$  due to the electroneutrality of  $\sigma_{R}^{S}$ .

 $\overline{\sigma}^{\mathcal{S}}(\mathbf{k}_{xy}) = \sigma^{\mathcal{S}}_{Ay} 4\pi^2 \delta^{(2)}(\mathbf{k}_{xy}) + \overline{\sigma}^{\mathcal{S}}_{\mathbf{R}}(\mathbf{k}_{xy}),$ 

where  $\delta^{(2)}$  is the two-dimensional Dirac function. Note that

where  $\sigma_{Av}^{S}$  is the average surface charge density defined as

$$\sigma_{\mathrm{Av}}^{\mathcal{S}} = \lim_{\mathcal{A} \to \infty} \mathcal{A}^{-1} \int d\mathbf{r}_{xy} \sigma^{\mathcal{S}}(\mathbf{r}_{xy}) = \lim_{\mathcal{A} \to \infty} \mathcal{A}^{-1} \overline{\sigma}^{\mathcal{S}}(\mathbf{0})$$

and  $\sigma_{R}^{S}(\mathbf{r}_{xy})$  is the remainder of surface charge distribution which is net electroneutral. Since  $\sigma_{Av}^{S}$  is a uniform surface charge den-

By inserting  $\widetilde{\sigma}_{w}(\mathbf{k}) = \overline{\sigma}^{\mathcal{S}}(\mathbf{k}_{xy})$  into Eq. (68) we obtain

$$\begin{split} \psi_{w}^{\sigma}(\mathbf{r}) &\sim \frac{1}{\mathcal{E}_{r}^{\text{eff}}\varepsilon_{0}(2\pi)^{3}} \int d\mathbf{k}_{xy} \int dk_{z} \frac{\overline{\sigma}^{\mathcal{S}}(\mathbf{k}_{xy})}{\kappa^{2} + k_{xy}^{2} + k_{z}^{2}} e^{i(\mathbf{k}_{xy} \cdot \mathbf{r}_{xy} + k_{z}z)} \quad \text{when } z \to \infty \\ &= \frac{1}{\mathcal{E}_{r}^{\text{eff}}\varepsilon_{0}8\pi^{2}} \int d\mathbf{k}_{xy} \overline{\sigma}^{\mathcal{S}}(\mathbf{k}_{xy}) \frac{e^{-z[\kappa^{2} + k_{xy}^{2}]^{1/2}}}{[\kappa^{2} + k_{xy}^{2}]^{1/2}} e^{i\mathbf{k}_{xy} \cdot \mathbf{r}_{xy}}, \end{split}$$
(71)

sity we have in Fourier space

where  $k_{xy} = |\mathbf{k}_{xy}|$  and the last equality follows from the fact that the inverse one-dimensional FT of  $1/(a^2 + k_z^2)$  is equal to  $\exp(-a|z|)/2a$  when a > 0 (applied for the case  $a^2 = \kappa^2 + k_{xy}^2$  and with z > 0). By breaking out a factor  $\exp(-\kappa z)/\kappa$  to the outside of the integral and inserting Eq. (70), we obtain when  $z \to \infty$ 

$$\begin{split} \psi_{w}^{\sigma}(\mathbf{r}) &\equiv \psi_{w}^{\sigma}(\mathbf{r}_{xy}, z) \quad \sim \quad \frac{e^{-\kappa z}}{\kappa \mathcal{E}_{r}^{\text{eff}} \varepsilon_{0} 8\pi^{2}} \int d\mathbf{k}_{xy} \left[ \sigma_{\text{Av}}^{\mathcal{S}} 4\pi^{2} \delta^{(2)}(\mathbf{k}_{xy}) + \overline{\sigma}_{\text{R}}^{\mathcal{S}}(\mathbf{k}_{xy}) \right] F(z, k_{xy}) e^{i\mathbf{k}_{xy} \cdot \mathbf{r}_{x}} \\ &= \quad \frac{e^{-\kappa z}}{\kappa \mathcal{E}_{r}^{\text{eff}} \varepsilon_{0} 8\pi^{2}} \left[ \sigma_{\text{Av}}^{\mathcal{S}} 4\pi^{2} + \int d\mathbf{k}_{xy} \overline{\sigma}_{\text{R}}^{\mathcal{S}}(\mathbf{k}_{xy}) F(z, k_{xy}) e^{i\mathbf{k}_{xy} \cdot \mathbf{r}_{xy}} \right] \end{split}$$

where  $F(z,k_{xy}) = \exp(-\kappa z [(1+k_{xy}^2/\kappa^2)^{1/2}-1])/(1+k_{xy}^2/\kappa^2)^{1/2}$  and the last equality follows from the fact that F(z,0) = 1. Note that the *x* and *y* dependence of  $\psi_w^{\sigma}(\mathbf{r})$  for large *z* originates solely from the term with  $\overline{\sigma}_R^S$ . When  $k_{xy} \neq 0$  we have  $F(z,k_{xy}) \to 0$  exponentially fast when  $z \to \infty$ . Since  $\overline{\sigma}_R^S(\mathbf{0}) = 0$ , the integral with  $\overline{\sigma}_R^S$  goes to zero in this limit and it follows that

$$\psi_{w}^{\sigma}(\mathbf{r}) \sim \frac{\sigma_{Av}^{S}}{2\kappa \mathcal{E}_{r}^{\text{eff}} \varepsilon_{0}} e^{-\kappa z} \quad \text{when } z \to \infty \text{ (only surface charges).}$$
(72)

Thus the *x* and *y* dependence of  $\psi_w^{\sigma}$  vanishes for large *z* and the limiting form of the screened potential from a nonuniform surface charge density is the same as from a uniformly smeared out one.

When the surface structure is periodic,  $\overline{\sigma}^{S}(\mathbf{k}_{xy})$  is equal to an infinite sum of Dirac delta functions located at the lattice points of the reciprocal lattice of this structure. From Eq. (71) follows that the (x, y) dependent part of  $\psi_w^{\sigma}$  decays like  $\exp[-z[\kappa^2 + s_1^2]^{1/2}]$  in the *z* direction, where  $s_1$  is equal to the  $k_{xy}$  value of the nonzero reciprocal lattice point(s) closest to  $\mathbf{k}_{xy} = 0$ . Thus the corresponding decay length is only a fraction of  $\lambda = \kappa^{-1}$ , so the *x* and *y* dependence vanishes quite quickly when *z* is increased.

The result (72) can easily be generalized and applied to  $\psi_w^{\sigma}$  from Eq. (67) for a general  $\sigma_w(\mathbf{r})$ , which is zero outside the wall, i.e., for z > 0. First, if there is a surface charge density distribution located at z = z' instead of at z = 0, the potential in this case is obtained from Eq. (72) by replacing  $\exp(-\kappa z)$  by  $\exp(-\kappa(z-z'))$  in the formula. Next, let us consider the contribution to the potential from  $\sigma_w(\mathbf{r}') \equiv \sigma_w(\mathbf{r}'_{xy}, z')$  in the interval (z', z' + dz') for an infinitesimally small dz', that is, from the surface charge distribution  $\sigma_w(\mathbf{r}'_{xy}, z')dz'$ . This contribution equals that in Eq. (72) with  $\exp(-\kappa(z-z'))$  inserted and with  $\sigma_{Av}^S$  replaced by the appropriate average density, i.e.,  $\lim_{A\to\infty} A^{-1} \left[ \int d\mathbf{r}'_{xy} \sigma_w(\mathbf{r}'_{xy}, z') dz'$ . It follows that the entire  $\psi_w^{\sigma}(\mathbf{r})$  can be obtained as an integral over z' with

all such contributions for  $z' \leq 0$ 

$$\psi^{\sigma}_{w}(\mathbf{r}) \sim \frac{1}{2\kappa \mathcal{E}^{\text{eff}}_{r} \varepsilon_{0}} \int_{-\infty}^{0} dz' \left[ \lim_{\mathcal{A} \to \infty} \frac{1}{\mathcal{A}} \int d\mathbf{r}'_{xy} \sigma_{w}(\mathbf{r}'_{xy}, z') \right] e^{-\kappa(z-z')}.$$

when  $z \rightarrow \infty$ . We can write this as

$$\Psi_{w}^{\sigma}(\mathbf{r}) \sim \frac{\sigma_{cAv}^{S}}{2\kappa \mathcal{E}_{r}^{eff} \varepsilon_{0}} e^{-\kappa z} \quad \text{when } z \to \infty,$$
(73)

where we have defined the composite average (cAv) surface charge density

$$\sigma_{cAv}^{S} = \lim_{\mathcal{A} \to \infty} \frac{1}{\mathcal{A}} \int d\mathbf{r}' \sigma_{w}(\mathbf{r}') e^{\kappa z'}$$
(74)

and the z' integration is done for  $z' \leq 0$  (where  $\sigma_w(\mathbf{r}') \neq 0$ ). Note that the dependence of  $\sigma_w(\mathbf{r}')$  on z' affects the value of the potential for large z, but the x' and y' dependencies of  $\sigma_w(\mathbf{r}')$  do not (in the limit  $z \to \infty$ ).

Finally, the potential  $\psi_w(\mathbf{r})$  from the dressed surface charge distribution  $\rho_w^*(\mathbf{r})$  given by Eq. (53) is obviously, in analogy to Eqs.

(73) and (74), decaying like

$$\Psi_{w}(\mathbf{r}) \sim \frac{\sigma^{\mathcal{S}\mathrm{eff}}}{\kappa \mathcal{E}_{r}^{\mathrm{eff}} \varepsilon_{0}} e^{-\kappa z} \quad \mathrm{when} \ z \to \infty,$$
(75)

where the effective surface charge density is given by

$$\sigma^{Seff} = \lim_{\mathcal{A} \to \infty} \frac{1}{2\mathcal{A}} \int d\mathbf{r}' \rho_w^*(\mathbf{r}') e^{\kappa z'}$$
(76)

with integration over the whole space. We have moved the factor 1/2 to the definition of  $\sigma^{Seff}$  for reasons explained in the main text. The integral converges in the limit  $z' \to \infty$  since  $\rho_w^*$  decays fast to zero in the cases considered here.

These results apply also for the case of complex-valued decay parameter  $\kappa = \kappa_{\Re} \pm i\kappa_{\Im}$  provided one adds the contributions to  $\psi_w$  from each of these two  $\kappa$  values as explained in the main text. The prefactor  $\sigma^{Seff}$  of each term is a complex quantity, but when the the two terms are added, the prefactor of the sum becomes real and contributes to the phase of the oscillation, so the actual effective surface charge density is real. Also in this case, the *x* and *y* dependence of  $\psi_w$  vanish in the limit  $z \to \infty$ . This follows from the fact that the factor  $\exp(-z(\kappa^2 + k_{xy}^2)^{1/2})$  in Eq. (71) decays faster than  $\exp(-\kappa z) \equiv \exp(-\kappa_{\Re} z) \exp(\mp i\kappa_{\Im} z)$  when  $k_{xy} \neq 0$  since the real part of  $((\kappa_{\Re} \pm i\kappa_{\Im})^2 + k_{xy}^2)^{1/2}$  then is greater than  $\kappa_{\Re}$ .

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