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# Screened Coulomb potential and the renormalized charges of ions and molecules in electrolyte solutions

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## Abstract

We consider solutions that consist of solute and solvent molecules of arbitrary sizes, shapes and internal charge distributions. The free energy of interaction (the potential of mean force) between the molecules is analysed in terms of a screened Coulomb potential and renormalized charge distributions of the molecules. The emphasis in this work is to bring out a simple physical interpretation of the theory, but the treatment is based on exact statistical mechanical theory without any approximations. The results thereby are the true properties of the system for given pair interaction potentials between the constituent particles. In general, the electric potential from any molecule in the solution can be exactly obtained for all distances by using a (generalized) screened Coulomb potential, provided the source charges constitute a renormalized charge distribution of the molecule. When charge renormalization is done consistently, macroions, small ions and solvent molecules are treated in fundamentally the same manner and all particles acquire renormalized charge distributions that generally are different from their actual (bare) distributions. The electrostatic free energy of interaction is given by the interaction between the renormalized charge distributions of the molecules as mediated by the screened Coulomb potential. The exact formalism is also used for the primitive model of electrolytes. The concepts in the general theory are illustrated by expressing the Poisson–Boltzmann and hypernetted chain (HNC) approximations in this alternative framework. Conditions are given under which the exact theory predicts the existence of attractive electrostatic interaction between two identical particles at large distances from each other.

## 1. Introduction

The concept of screened Coulomb potential is important for our understanding of electrolyte systems like, for example, simple electrolyte solutions, colloidal dispersions and macromolecular solutions. Usually, the screened Coulomb potential is taken to mean the

potential from a charge in an electrolyte as predicted by the Debye–Hückel theory of electrolyte solutions. In the application of this potential to calculate interactions between charged particles or functional groups, it is common to use the actual charges of the various entities to obtain the electrostatic interaction energy. As we will see, this way of using a screened Coulomb potential is inconsistent in general. In the current work we show how the screened Coulomb potential can be generalized in exact statistical mechanics of electrolyte systems with molecular solvent. The electrostatic potential from a charged molecule and the electrostatic free energy of interaction between two molecules can then be obtained from the generalized screened Coulomb potential and *renormalized* charge distributions of the various particles. Thereby, macroions, small ions and solvent molecules are treated in fundamentally the same manner. In the general theory there are no limitations on the sizes and shapes of the particles. Many-body correlations and solvation effects (including, for instance, dielectric saturation) are implicitly contained in the treatment. For simplicity we will only treat rigid particles that interact electrostatically and with short-ranged, non-power-law pair interactions like, for example, hard-core potentials. The molecules are, furthermore, assumed to be non-polarizable in the present treatment. We will only consider homogeneous solutions.

The theory of polar molecular liquids and electrolyte systems has a long history and a vast literature. The current paper is not intended to give a fair coverage of this field, but only to present how it is possible to formulate an exact, but physically transparent, formalism that brings out key elements of these kinds of systems: the ‘dressed molecule theory’ [1]. For some key references of the background literature, see papers cited in [1].

In the exposition of the theory presented in this paper we will emphasize the physical interpretation of the various theoretical relationships while keeping the statistical mechanics at a very basic level (for completeness some less basic statistical mechanical arguments are included in an appendix). Note, however, that our analysis is based on exact statistical mechanical theory without any approximations. The results are therefore genuine properties of the system for given intermolecular pair interaction potentials. For a more complete treatment of the theory (including formulas to be used in practical applications) we refer to our earlier publications [1–3] and references therein.

An exact statistical mechanical analysis of the problem is highly desirable since it provides:

- (i) exact results for a given system that have to be fulfilled in any further correct developments and applications,
- (ii) general relationships between various properties of the system,
- (iii) equations that can be used to calculate such properties and
- (iv) a correct conceptual framework for an understanding of the properties of the system, at least provided the analysis is physically transparent.

Due to the general nature of the analysis it is not always possible to specify the precise conditions under which some of the results are valid for every conceivable system. For example, results like some decay laws of the electrostatic potential for large distances are, as we will see, valid provided the electrolyte concentration is not too high. This means that there will exist a finite concentration below which the statement is correct—the precise range of validity is system dependent and has, in most cases, to be explored by numerical treatments. For such treatments we refer to the cited literature and references therein.

The outline of this work is as follows. We will first give the general definition of the screened Coulomb potential. The renormalized charge distribution of a molecule is then defined so the application of the screened Coulomb potential with the renormalized charge as a source gives the actual electrostatic potential from the molecule. We will proceed to show how these entities appear naturally in the intermolecular free energy of interaction

(the potential of mean force). We will find that the electrostatic part of this free energy is given by the interaction between the renormalized charge distributions of the molecules as mediated by the screened Coulomb potential. This is a highly non-trivial result, that shows that our way of defining renormalized charge and screened Coulomb potential is fundamentally correct. Other charge renormalization schemes do not share these properties. To illustrate the concepts we will show how the Poisson–Boltzmann and the hypernetted chain approximations can be formulated using the formalism. It is also shown how effective charges appear in the exact theory.

## 2. The unit screened Coulomb potential

Let  $\psi_{[q]}(r)$  denote the electrostatic potential at distance  $r$  from a point particle with charge  $q$  (a ‘point charge’  $q$ ). When the charge is immersed in pure solvent the potential decays for large  $r$  as [4, 5]

$$\psi_{[q]}(r) \sim \frac{q\varphi_{\text{Coul}}(r)}{\epsilon_r} = \frac{q}{4\pi\epsilon_0\epsilon_r r}, \quad r \rightarrow \infty \text{ (pure solvent)}, \quad (1)$$

where  $\varphi_{\text{Coul}}(r) = 1/(4\pi\epsilon_0 r)$  is the Coulomb potential from a unit point charge in vacuum,  $\epsilon_0$  is the permittivity of vacuum and  $\epsilon_r$  is the dielectric constant (relative permittivity) of the solvent. Note that the potential is proportional to  $q$ . This holds irrespectively of the magnitude of  $q$ , so, for example, the potential from a unit point charge is  $\varphi_{\text{Coul}}(r)/\epsilon_r$  for large  $r$  and is equal to  $\psi_{[q]}(r)/q$  there. The dielectric constant only characterizes the propagation of the electrostatic potential over large distances, so the potential from a unit point charge is not given by  $\varphi_{\text{Coul}}(r)/\epsilon_r$  for small  $r$ . In fact, the  $q$  dependence of  $\psi_{[q]}$  is in general non-linear for small  $r$  where the electric field from the charge is large. This is due to dielectric saturation and similar effects. Thus, if one wants to find a ‘unit’ potential for the fluid that corresponds to  $\varphi_{\text{Coul}}(r)$  in vacuum,  $\psi_{[q]}(r)/q$  is not a suitable choice since it depends on  $q$ . It is only in the limit of small  $q$  that  $\psi_{[q]}(r)/q$  is everywhere independent of  $q$ .

To obtain a unit potential  $\phi_{\text{Coul}}^0$  that is of use for all  $r$  values in the fluid we therefore define

$$\phi_{\text{Coul}}^0(r) = \lim_{q \rightarrow 0} \frac{\psi_{[q]}(r)}{q}. \quad (2)$$

This definition implies that the potential from a point particle with an infinitesimally small charge  $\delta q$  is given by  $\psi_{[\delta q]}(r) = \delta q \phi_{\text{Coul}}^0(r)$  for all  $r$ . Thus  $\phi_{\text{Coul}}^0$  describes the linear response of the fluid. For large  $r$  it follows from equation (1) that

$$\phi_{\text{Coul}}^0(r) \sim \frac{\varphi_{\text{Coul}}(r)}{\epsilon_r} = \frac{1}{4\pi\epsilon_0\epsilon_r r}, \quad r \rightarrow \infty \text{ (pure solvent)}. \quad (3)$$

In an electrolyte solution the electrostatic potential is exponentially screened. In the limit of infinite dilution of the electrolyte the potential from a point charge  $q$  decays like  $\psi_{[q]}(r) \sim qe^{-\kappa_D r} \varphi_{\text{Coul}}(r)/\epsilon_r$  for large  $r$  [6–8], which differ by the factor  $e^{-\kappa_D r}$  from the previous case. The decay parameter  $\kappa_D$  is the Debye parameter ( $\kappa_D^{-1}$  is the Debye length) defined from  $\kappa_D^2 = \sum_i n_i q_i^2 / (\epsilon_0 \epsilon_r k_B T)$ , where  $n_i$  is the number density and  $q_i$  the charge of species  $i$ , the sum is taken over all ionic species,  $k_B$  is Boltzmann’s constant and  $T$  the absolute temperature. For small  $r$  the situation is similar as for pure solvent and we define  $\phi_{\text{Coul}}^0$  as before (equation (2)) for all  $r$ . In this case

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

Note that in both cases considered so far  $\psi_{[q]}(r) \sim q\phi_{\text{Coul}}^0(r)$  for large  $r$ .

Let us now consider an electrolyte solution at finite concentration. We define the new  $\phi_{\text{Coul}}^0$  from equation (2) by using the potential  $\psi_{[q]}(r)$  obtained at finite concentration. Again,

the potential from an infinitesimally small point charge  $\delta q$  obeys  $\psi_{[\delta q]}(r) = \delta q \phi_{\text{Coul}}^0(r)$  for all  $r$ . Provided the electrolyte concentration is not too high  $\phi_{\text{Coul}}^0(r)$  still decays like a Yukawa function  $\exp(-\kappa r)/r$  where  $\kappa$  is a constant [1]

$$\phi_{\text{Coul}}^0(r) \sim \frac{e^{-\kappa r} \varphi_{\text{Coul}}(r)}{E_r} = \frac{e^{-\kappa r}}{4\pi\epsilon_0 E_r r}, \quad r \rightarrow \infty \text{ (finite concentration)}, \quad (5)$$

but the decay parameter is not equal to the Debye parameter,  $\kappa \neq \kappa_D$ , and  $E_r$  in the denominator differs from the dielectric constant  $\epsilon_r$  of the pure solvent. The product  $\epsilon_0 E_r$  is an effective permittivity of the electrolyte solution and it contains contributions from both solvent molecules and ions.

In this case, the potential from a point charge,  $\psi_{[q]}(r)$ , is no longer proportional to  $q$  (except in the limit of small  $q$ , the linear response regime). The attraction of counterions and repulsion of coions and other effects near the point charge leads in general to a non-linear dependence of  $\psi_{[q]}(r)$  on  $q$  even for large  $r$  values. The potential still decays like a Yukawa function but with a prefactor different from  $q$

$$\psi_{[q]}(r) \sim q^0 \phi_{\text{Coul}}^0(r) \sim \frac{q^0 e^{-\kappa r}}{4\pi\epsilon_0 E_r r}, \quad r \rightarrow \infty \text{ (finite concentration)}. \quad (6)$$

The quantity  $q^0$  can be interpreted as an effective charge, which depends in a non-linear manner on the actual (bare) charge  $q$ . In the limit  $q \rightarrow 0$  we see that  $q^0 \sim q$  (linear response regime) and, furthermore, from equation (4) it follows that  $E_r \rightarrow \epsilon_r$  and  $q^0 \rightarrow q$  (for all  $q$ ) in the limit of infinite dilution.

The effective charge  $q^0$  contains in general contributions from both ions and solvent molecules. The latter contribute to the effective charge despite the fact that they are electroneutral, which is in stark contrast to the pure solvent case where they only contribute to  $\epsilon_r$  in equation (1). The reason for the difference is that the Coulomb potential decays like  $1/(4\pi\epsilon_0\epsilon_r r)$  in pure solvent, which implies that the contributions from the internal charge distribution of an electroneutral molecule cancel in the leading  $1/r$  term. There remain only contributions to higher order terms (dipolar, quadrupolar etc) which decay faster with distance. In an electrolyte solution the decay is exponential, which implies that the contributions from the positive and negative charges of an oriented solvent molecule in general no longer cancel exactly in the leading term, but instead give a net contribution that decays for large  $r$  in the same manner as the contribution from an ion, that is, like  $\exp(-\kappa r)/r$ . This is the reason why both ions and electroneutral molecules contribute to the net effective charge.

In a completely analogous manner one can define the ‘effective point charge’ of a spherical ion of species  $i$  in an electrolyte solution. The potential  $\psi_i(r)$  at distance  $r$  from the centre of the  $i$  ion decays like  $\psi_i(r) \sim q_i^0 \phi_{\text{Coul}}^0(r)$  for large  $r$ , where the prefactor  $q_i^0$  in general depends non-linearly on the bare ionic charge  $q_i$ . It will also depend in a non-trivial fashion on the size of the ion. We define  $q_i^0$  to be the effective point charge of the ion (there is also a phase factor involved when  $\phi_{\text{Coul}}^0(r)$  is oscillatory, which can happen at high concentrations). Usually  $q_i^0$  is non-zero even if  $q_i$  is zero, so an uncharged hard sphere in an electrolyte will in general behave like a charged particle. As regards non-spherical particles, the decay of the potential cannot be described simply by an effective point charge since there is an angular dependence too; see below.

We will call  $\phi_{\text{Coul}}^0(r)$  the ‘unit screened Coulomb potential’, and as we will see it plays a fundamental role in the theory of electrolyte systems. Remember that it is defined for all  $r$ . In general, it is only for large  $r$  values that it has a simple functional form like in equation (5).

The primitive model of electrolytes is commonly used in electrolyte theory. In this model the ions are charged hard spheres and the solvent is treated like a dielectric continuum, which is characterized only by its dielectric constant  $\epsilon_r$ . Equations (1) and (3) for pure solvent are

then assumed to be identities valid for all  $r$  as an approximation. Otherwise, all results above remain valid as they stand (except, of course, the discussion about various contributions from solvent molecules). We will use this model as a special case to illustrate some properties of the general theory.

As we have seen, the decay of  $\phi_{\text{Coul}}^0(r)$  is like a Yukawa function for large distances only. Equation (5) then gives just the leading term in the asymptotic decay of  $\phi_{\text{Coul}}^0(r)$ . For smaller distances the  $r$  dependence is more complicated and higher order terms that decay faster with  $r$  cannot be neglected. In many cases the second leading term when  $r \rightarrow \infty$  is another Yukawa function term with a decay parameter  $\kappa'$  that is larger than  $\kappa$  (decay length  $1/\kappa' < 1/\kappa$ ) [9]. Then

$$\phi_{\text{Coul}}^0(r) \sim \frac{e^{-\kappa r} \varphi_{\text{Coul}}(r)}{E_r} + \frac{e^{-\kappa' r} \varphi_{\text{Coul}}(r)}{E_r'}, \quad r \rightarrow \infty, \quad (7)$$

where the constant  $E_r'$  is always a *negative* number. For example, for 1:2 electrolytes in aqueous solutions at room temperature  $\kappa'$  and  $\kappa$  are not too different in a fairly wide concentration interval [9] and both terms can play important roles as we will see later. When the concentration is increased  $\kappa'$  and  $\kappa$  tend to each other and at some point they become equal. At higher concentrations  $\phi_{\text{Coul}}^0(r)$  decays in an exponentially damped and oscillatory manner (then  $\kappa'$  and  $\kappa$  are complex numbers that are complex conjugates to each other and the sum of the two terms in equation (7) constitutes an exponentially damped, sinusoidal function). For small  $r$  many additional terms contribute to  $\phi_{\text{Coul}}^0(r)$ .

The Poisson–Boltzmann (PB) approximation, which is based on the primitive model, is the classical theory for electrolyte systems and is still commonly used. In this approximation we have

$$\phi_{\text{Coul}}^{0,\text{PB}}(r) = \frac{e^{-\kappa_{\text{D}} r} \varphi_{\text{Coul}}(r)}{\epsilon_r} = \frac{e^{-\kappa_{\text{D}} r}}{4\pi\epsilon_0\epsilon_r r} \quad (8)$$

for *all*  $r$  and for *all* electrolyte concentrations (cf equation (4), which in general is only valid for *large* distances in *dilute* solutions). The function  $\phi_{\text{Coul}}^{0,\text{PB}}(r)$  is commonly referred to as ‘the screened Coulomb potential’ in the literature, so our concept of the ‘unit screened Coulomb potential’ is a generalization of this function to the general exact case.

### 3. Renormalized charge distributions

#### 3.1. Primitive model

Consider a particle of species  $i$  in an electrolyte solution. It can, for example, be a spherical colloidal particle or a simple ion. We will take  $r$  as the distance from its centre. The mean electrostatic potential  $\psi_i(r)$  from this particle originates from the charge of the particle and the surrounding ‘ion atmosphere’. The charge distribution of the latter,  $\rho_i^{\text{atm}}(r)$ , is mainly caused by attraction of counterions and repulsion of coions (i.e. the ‘polarization response’ of the surrounding solution due to interactions with the particle). The total charge distribution  $\rho_i(r)$  associated with the particle consists of  $\rho_i^{\text{atm}}(r)$  and the internal charge distribution of the central ion (e.g. a surface charge density or a point charge at the centre) described by a charge density  $\sigma_i(r)$ . Thus we have  $\rho_i = \rho_i^{\text{atm}} + \sigma_i$ . The electrostatic potential  $\psi_i$  is given by Coulomb’s law

$$\psi_i(r_{12}) = \int d\mathbf{r}_3 \rho_i(r_{13}) \phi_{\text{Coul}}(r_{32}), \quad (9)$$

where  $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$  and  $\phi_{\text{Coul}}(r) = \varphi_{\text{Coul}}(r)/\epsilon_r$  is the Coulomb potential appropriate for the dielectric continuum solvent used in the primitive model. The  $i$  particle is placed at  $\mathbf{r}_1$  and we look at the potential at  $\mathbf{r}_2$ .

We now want to use the unit screened Coulomb potential  $\phi_{\text{Coul}}^0$  rather than the ordinary Coulomb potential  $\phi_{\text{Coul}}$  to describe the electrostatics in the system. To obtain the *same* potential  $\psi_i(r)$  we can, of course, not just insert  $\phi_{\text{Coul}}^0$  instead of  $\phi_{\text{Coul}}$  in equation (9). We also have to replace  $\rho_i(r)$  by some other function, which we will denote  $\rho_i^0(r)$ , that is,

$$\psi_i(r_{12}) = \int d\mathbf{r}_3 \rho_i^0(r_{13}) \phi_{\text{Coul}}^0(r_{32}). \quad (10)$$

The quantity  $\rho_i^0(r)$  constitutes a *renormalized charge density* that is appropriate for use with the unit screened Coulomb potential and is uniquely defined by equation (10). Note that the electrostatic potential is obtained for all  $r_{12}$  from equation (10). Both  $\rho_i$  and  $\rho_i^0$  includes the internal charge distribution of the particle. The part of  $\rho_i^0$  in excess of the internal charge is denoted the ‘dress’ of the ion, so  $\rho_i^0$  is also called the *dressed ion* charge density. To make our definition of  $\rho_i^0(r)$  more concrete, let us see how this works out in the PB approximation.

### 3.2. Poisson–Boltzmann approximation

The unit screened Coulomb potential in this case is given by equation (8), i.e. a simple Yukawa function for all  $r$ . We first consider a point particle with charge  $q$  at the origin. As we have seen, the potential  $\psi_{[q]}^{\text{PB}}(r)$  from the charge  $q$  is equal to the product  $q\phi_{\text{Coul}}^{0,\text{PB}}(r)$  provided  $q$  is very small. This is the result of the linear PB (LPB) approximation, also called the Debye–Hückel approximation. The potential from the *linear* polarization response of the electrolyte solution around the point charge is included in  $q\phi_{\text{Coul}}^{0,\text{PB}}(r)$ , i.e. the contributions from the ion atmosphere around  $q$  as calculated in the linear approximation. This feature is, in fact, general, so  $\phi_{\text{Coul}}^0$  as defined by equation (2) will always include the linear response contributions to the potential. In the LPB approximation we have for  $r > 0$

$$\rho^{\text{atm,PB}} = -\epsilon_0 \epsilon_r \nabla^2 \psi^{\text{PB}} \approx -\epsilon_0 \epsilon_r \kappa_D^2 \psi^{\text{PB}} \quad (\text{linear PB approximation}), \quad (11)$$

where we have used Poisson’s equation and the linearized PB equation. The rhs of equation (11) gives the linear polarization response in terms of the total potential  $\psi^{\text{PB}}$ , which results from all charges including the polarization.

If  $q$  is not small the potential is not given by  $q\phi_{\text{Coul}}^{0,\text{PB}}(r)$  and instead the non-linear PB approximation has to be used. The potential  $\psi_{[q]}^{\text{PB}}(r)$  is given by equation (9) (with subscript  $[q]$  instead of  $i$ ), where we have inserted total charge distribution  $\rho_{[q]}^{\text{PB}}(r)$  as calculated in the non-linear PB approximation. If we want to calculate the potential by using the unit screened Coulomb potential instead, equation (10), the linear part of the polarization response is taken care of by  $\phi_{\text{Coul}}^{0,\text{PB}}$  while the non-linear contributions must be described by  $\rho_{[q]}^{0,\text{PB}}$ . Thus the difference between  $\rho_{[q]}^{\text{PB}}$  and  $\rho_{[q]}^{0,\text{PB}}$  is that the latter does not include the linear part of the response. Explicitly, we have

$$\rho^{0,\text{PB}} = \rho^{\text{PB}} + \epsilon_0 \epsilon_r \kappa_D^2 \psi^{\text{PB}} \quad (\text{nonlinear PB approximation}), \quad (12)$$

where the second term in the rhs removes the linear part. Note that both  $\rho_{[q]}^{\text{PB}}(r)$  and  $\rho_{[q]}^{0,\text{PB}}(r)$  include the central charge  $q$ .

The result (12) also applies to the charge distributions associated with a particle of species  $i$ . The renormalized charge distribution  $\rho_i^{0,\text{PB}}$  outside the hard core of the particle is equal to  $\rho_i^{\text{atm,PB}} + \epsilon_0 \epsilon_r \kappa_D^2 \psi_i^{\text{PB}}$ . Inside the core where  $\rho_i^{\text{atm}} = 0$ , the function  $\rho_i^{0,\text{PB}}$  consists of the sum of the internal charge distribution of the particle and  $\epsilon_0 \epsilon_r \kappa_D^2 \psi_i^{\text{PB}}$ , which is non-zero since  $\psi_i^{\text{PB}}$  is non-zero there. The latter contribution to  $\rho_i^{0,\text{PB}}$  is a nominal charge distribution that makes sure that  $\rho_i^{0,\text{PB}}$  gives a potential that arises from a system that fulfils the condition  $\rho_i^{\text{atm}} = 0$  inside the core (the ‘core condition’).

As an illustration of how this nominal distribution works, consider the LPB approximation for the case of a central ion with core radius  $a$  and a point charge  $q_i$  at its centre. In this case  $\rho_i^{0,\text{PB}}(r)$  is zero outside the core, while it is  $\epsilon_0\epsilon_r\kappa_D^2\psi_i^{\text{PB}}(r)$  for  $0 < r < a$ . It also includes the point charge  $q_i$  at  $r = 0$ . If the contribution  $\epsilon_0\epsilon_r\kappa_D^2\psi_i^{\text{PB}}(r)$  was not present, only the point charge would remain and equation (10) would yield  $\psi_i^{\text{PB}}(r) = q_i\phi_{\text{Coul}}^{0,\text{PB}}(r)$ , which is not correct. The correct potential in the LPB case is  $\psi_i^{\text{PB}}(r) = q_i^{0,\text{LPB}}\phi_{\text{Coul}}^{0,\text{PB}}(r)$  for  $r > a$ , where  $q_i^{0,\text{LPB}} = q_i \exp(\kappa_D a)/(1 + \kappa_D a)$  is the effective point charge that includes the finite ion size effect. One can easily check that the correct result is in agreement with equation (10) and that the deviation of  $q_i^{0,\text{LPB}}$  from  $q_i$  results from the term  $\epsilon_0\epsilon_r\kappa_D^2\psi_i^{\text{PB}}(r)$  in the core region. Likewise, in the non-linear PB case the nominal charge distribution from this term inside the core assures that the core condition is fulfilled.

We now leave the PB approximation and return to the general, exact case for a primitive model of section 3.1. Then  $\phi_{\text{Coul}}^0(r)$  is not a simple Yukawa potential. Furthermore, the linear response part of  $\rho_i^0$  is not as simple as in equation (12), but it is still linear in  $\psi_i$  (it is a linear functional of  $\psi_i$  where the kernel is a linear response function [1, 3]). Also in this case the renormalized charge distribution contains the nonlinear parts of the polarization response and a nominal charge distribution inside the core that takes care of the core condition.

From our definitions of screened Coulomb potential and renormalized charge density it is so far not clear whether these quantities have any fundamental roles. This will, however, be apparent when we treat the interaction free energy between molecules in the solution. As we will see, the electrostatic part of the interaction free energy equals the screened Coulomb interaction between the renormalized charge distribution  $\rho^0$  of the two molecules. Before we do this we will give the definition of  $\rho^0$  for the general case of systems with molecular solvent.

### 3.3. General case with molecular solvent

Consider a molecule of species  $i$  located at the origin (its centre of mass is at the origin). It can be a solute or a solvent molecule. We assume for simplicity that it is rigid and placed in a certain orientation relative to the frame of reference. The orientation is described by a variable  $\omega$ . The molecule has an internal charge distribution  $\sigma_{i,\omega}(\mathbf{r})$ , i.e. the charge density at coordinate  $\mathbf{r}$  when the  $i$  molecule is in orientation  $\omega$ . The interactions between this molecule and the surrounding solvent and solute molecules polarize the surroundings by repelling and/or attracting ions and affecting the locations and orientations of solvent molecules. The charge distribution of this ‘ion and solvent atmosphere’ around the molecule is denoted  $\rho_{i,\omega}^{\text{atm}}(\mathbf{r})$ . The total charge distribution  $\rho_{i,\omega}(\mathbf{r})$  associated with the molecule is the sum of these two,  $\rho_{i,\omega}(\mathbf{r}) = \sigma_{i,\omega}(\mathbf{r}) + \rho_{i,\omega}^{\text{atm}}(\mathbf{r})$ .

The electrostatic potential due to the molecule, including that from the polarized surroundings, is given by Coulomb’s law

$$\psi_{i,\omega}(\mathbf{r}_{12}) = \int d\mathbf{r}_3 \rho_{i,\omega}(\mathbf{r}_{13})\varphi_{\text{Coul}}(r_{32})$$

and, as before, we define the renormalized charge density  $\rho_{i,\omega}^0$  from

$$\psi_{i,\omega}(\mathbf{r}_{12}) = \int d\mathbf{r}_3 \rho_{i,\omega}^0(\mathbf{r}_{13})\phi_{\text{Coul}}^0(r_{32}) \quad (13)$$

where the unit screened Coulomb potential  $\phi_{\text{Coul}}^0(r)$  is that of the bulk solution as obtained from equation (2). Both  $\rho_{i,\omega}$  and  $\rho_{i,\omega}^0$  include the internal charge distribution  $\sigma_{i,\omega}$ . We denote  $\rho_{i,\omega}^0$  as the *dressed molecule* charge density.



#### 4. Intermolecular interaction (free) energy

##### 4.1. Poisson–Boltzmann approximation and its non-local correction

The interaction free energy (potential of mean force)  $w_{ij}(r)$  between two particles of species  $i$  and  $j$  in a fluid is in general defined from the relationship

$$g_{ij}(r) = e^{-\frac{w_{ij}(r)}{k_B T}},$$

where  $g_{ij}(r)$  is the radial distribution function (for simplicity in notation, we here assume that the particles are spherical). In the PB approximation the interaction free energy between the central particle (species  $i$ ) and an ion in the surrounding ion atmosphere (species  $j$ ) is given by  $w_{ij}^{\text{PB}}(r) = u_{ij}^{\text{short}} + \psi_i^{\text{PB}}(r)q_j$ , where  $u_{ij}^{\text{short}}$  is the short-ranged, non-electrostatic part of the pair interaction potential (here it is a hard-core potential). If we insert equation (10) we can write the electrostatic part of  $w_{ij}^{\text{PB}}(r)$  as

$$w_{ij}^{\text{el,PB}}(r_{12}) = \psi_i^{\text{PB}}(r_{12})q_j = \int d\mathbf{r}_3 \rho_i^{0,\text{PB}}(r_{13})\phi_{\text{Coul}}^{0,\text{PB}}(r_{32})q_j. \quad (14)$$

The physical interpretation of equation (14) is that  $w_{ij}^{\text{el,PB}}$  is the electrostatic interaction energy given by the screened Coulomb interaction between the dressed central particle ( $\rho_i^{0,\text{PB}}$ ) and the bare charge  $q_j$  of the  $j$  ion in the atmosphere. This clearly shows the unequal treatment of the central particle and the ions in the ion atmosphere. While the central particle is dressed, the ions in the atmosphere are without dress in the PB approximation. This leads to the well known deficiency that  $w_{ij}^{\text{PB}}(r) \neq w_{ji}^{\text{PB}}(r)$ , while it is required in the exact case that  $w_{ij}(r) = w_{ji}(r)$ .

A fundamentally correct way to remedy this deficiency is, as we will see below, to make the ions in the atmosphere dressed too. The electrostatic interaction energy between a dressed  $j$  ion and the potential  $\psi_i$  due to the  $i$  particle is given by

$$w_{ij}^{\text{el}}(r_{12}) = \int d\mathbf{r}_4 \psi_i(r_{14})\rho_j^0(r_{24}) = \int d\mathbf{r}_3 d\mathbf{r}_4 \rho_i^0(r_{13})\phi_{\text{Coul}}^0(r_{34})\rho_j^0(r_{24}), \quad (15)$$

where we have inserted equation (10). The rhs expresses that the screened Coulomb potential conveys the interaction between two dressed particles. All particles are treated in the same manner and the symmetry  $w_{ij}^{\text{el}}(r) = w_{ji}^{\text{el}}(r)$  is satisfied. It is a *nontrivial fact* that the free energy for the screened electrostatic pair interaction can be written as in equation (15); see below. This fact gives a fundamental argument for our definitions of screened Coulomb potential in equation (2) and renormalized charge density (dressed ion charge density) in equation (10). These definitions allow us to write equation (15)

$$w_{ij}^{\text{el}}(r_{12}) = \int d\mathbf{r}_3 \rho_i^0(r_{13})\psi_j(r_{23}) \quad (16)$$

where the roles of the two particles are changed; here it is the  $j$  particle that gives rise to the electrostatic potential. This would not be possible with some other definitions. Given that  $w_{ij}^{\text{el}}(r_{12})$  can be expressed by both the first equality in equations (15) and (16), there is no other option than to define the screened Coulomb potential such that the second equality in equation (15) is fulfilled. These requirements make  $\rho_i^0$ ,  $\rho_j^0$  and  $\phi_{\text{Coul}}^0$  uniquely defined and in accordance with our definitions above.

If we take, as an approximation,  $w_{ij} \approx u_{ij}^{\text{short}} + w_{ij}^{\text{el}}$  we obtain a symmetrical version of the PB approximation. This is an approximation because there are other interaction free energy contributions apart from the screened electrostatic one given by  $w_{ij}^{\text{el}}$ . Since the ions in the ion atmosphere interact non-locally (via their dress) with the potential from the central particle, we may call this approximation the *non-local PB approximation* [2]. We will not pursue this here, but instead turn to the exact case.

#### 4.2. General case in primitive model

The exact interaction free energy  $w_{ij}$  can be written as (cf the appendix)

$$w_{ij} = u_{ij}^{\text{short}} + w_{ij}^{\text{el}} + w_{ij}^{\text{dress}} + w_{ij}^{\text{bridge}}, \quad (17)$$

where  $w_{ij}^{\text{el}}$  is defined by equation (15),  $w_{ij}^{\text{dress}}$  contains non-electrostatic and indirect electrostatic effects from interactions between the dresses of the  $i$  and the  $j$  ions (it is defined in the appendix), and  $w_{ij}^{\text{bridge}}$  gives short-ranged contributions due to the most complicated effects of the many-particle correlations ( $w_{ij}^{\text{bridge}}$  is proportional to the so-called bridge function [10] of liquid state theory; see the appendix). In the hypernetted chain (HNC) approximation, which in many cases is an excellent approximation for electrolytes in the primitive model,  $w_{ij}^{\text{bridge}}$  is set equal to zero and one takes

$$w_{ij}^{\text{HNC}} = u_{ij}^{\text{short}} + w_{ij}^{\text{el}} + w_{ij}^{\text{dress}}.$$

In many important cases the electrostatic interactions dominate in the behaviour of the electrolyte system, in particular for large separations between the particles. This is the case provided the electrolyte concentration is not too high and then both  $w_{ij}^{\text{dress}}(r_{12})$  and  $w_{ij}^{\text{bridge}}(r_{12})$  are more short ranged than  $w_{ij}^{\text{el}}(r_{12})$ , so the latter dominates the decay behaviour of  $w_{ij}(r_{12})$  for large  $r_{12}$

$$w_{ij}(r_{12}) \sim \int \mathbf{dr}_3 \mathbf{dr}_4 \rho_i^0(r_{13}) \phi_{\text{Coul}}^0(r_{34}) \rho_j^0(r_{24}), \quad r_{12} \rightarrow \infty. \quad (18)$$

In many cases the rhs will give a dominant part of the interaction free energy for fairly short separations too. When  $\phi_{\text{Coul}}^0(r)$  decays as in equation (7) the leading two terms from equation (18) are given by [9]

$$w_{ij}(r_{12}) \sim \frac{q_i^0 q_j^0 e^{-\kappa r_{12}} \varphi_{\text{Coul}}(r_{12})}{E_r} + \frac{q_i'^0 q_j'^0 e^{-\kappa' r_{12}} \varphi_{\text{Coul}}(r_{12})}{E_r'}, \quad r_{12} \rightarrow \infty, \quad (19)$$

where  $q_l^0, l = i, j$ , is the effective charge introduced in section 2 and  $q_l'^0$  is an analogous quantity ('secondary effective charge') associated with the second leading term. One may call  $q_l^0$  the 'primary effective charge' when one needs to distinguish the two charges. Both  $q_l^0$  and  $q_l'^0$  are weighted integrals of the dressed ion charge distribution  $\rho_l^0(r)$  in three dimensions [9] (the weighting function is  $\sinh(kr)/(kr)$  with  $k = \kappa$  and  $k = \kappa'$  respectively). The effective charges reflect how strongly  $\rho_l^0(r)$  couple to these two leading decay modes of  $\phi_{\text{Coul}}^0(r)$  and hence  $q_l^0$  and  $q_l'^0$  represent different manifestations of the renormalized charge density expressed as effective point charges. Together, the two effective charges describe most features of the charge density profile and electrostatic potential for distances larger than a few ionic diameters from the particle surface in 1:2 electrolytes for several cases [9, 11]. The higher order terms, not shown in equation (19), decay faster than the two terms shown when  $r_{12} \rightarrow \infty$ .

For two particles of the same species,  $i = j$ , the first term in equation (19) will contain a factor  $(q_i^0)^2$  and is always repulsive since  $E_r > 0$ . Likewise, the second term will always be attractive in this case since  $E_r' < 0$ . For colloid particles in multivalent aqueous electrolytes at room temperature the effective charge  $q_l^0$  can change sign when the magnitude of the bare charge is increased. This is the phenomenon of 'overcharging' or 'effective charge reversal' that has been observed for a long time, but has lately received a lot of renewed interest. At the point of charge reversal  $q_i^0 = 0$  and the leading term is absent. At this point the second term becomes the dominant term when  $r_{12} \rightarrow \infty$  and hence there is a *long-ranged electrostatic attraction* between two equally charged particles! The properties of the two kinds of effective charges have been systematically investigated with accurate calculations for planar surfaces by Ulander *et al* [11].

### 4.3. Intermolecular interactions in electrolytes with molecular solvent

The result in equation (17) also applies for electrolytes with molecular solvent. For non-spherical molecules one must consider the orientations as well as the positions of the molecules. Consider an  $i$  molecule that is placed with its centre of mass at coordinate  $\mathbf{r}_1$  and has orientation  $\omega_1$  (relative to the laboratory frame of reference) and a  $j$  molecule that is placed at coordinate  $\mathbf{r}_2$  and has orientation  $\omega_2$ . Then the free energy of interaction between the particles is denoted  $w_{ij,\omega_1\omega_2}(\mathbf{r}_{12})$ . The various equations have to be generalized to include orientations in analogy to what is done in equation (13) (cf equation (20) below).

As before, in many important cases the electrostatic interactions dominate in the behaviour of the electrolyte system, in particular for large separations between the particles. This is, for example, the case for low electrolyte concentrations. Then  $w_{ij,\omega_1\omega_2}^{\text{el}}$  gives the leading contribution to the free energy of interaction for large separations and we have

$$w_{ij,\omega_1\omega_2}(\mathbf{r}_{12}) \sim \int d\mathbf{r}_3 d\mathbf{r}_4 \rho_{i,\omega_1}^0(\mathbf{r}_{13}) \phi_{\text{Coul}}^0(r_{34}) \rho_{i,\omega_2}^0(\mathbf{r}_{24}), \quad r_{12} \rightarrow \infty, \quad (20)$$

where  $\phi_{\text{Coul}}^0(r)$  is the unit screened Coulomb potential of the bulk solution, which only depends on the distance  $r$ . The rhs of equation (20) has exactly the same appearance as the normal Coulombic interaction energy between two charge distributions,  $\sigma_a(\mathbf{r}_{13})$  placed at  $\mathbf{r}_1$  and  $\sigma_b(\mathbf{r}_{24})$  placed at  $\mathbf{r}_2$ , interacting with the usual Coulomb potential  $\varphi_{\text{Coul}}(r_{34})$  in vacuum. The essential difference is that  $\rho^0$  and  $\phi_{\text{Coul}}^0$  include polarization and other correlation effects of the solution surrounding the molecules in accordance with the discussion in the previous sections. The effects of the molecular solvent are implicitly contained in these quantities. One can expect that the rhs of equation (20) in many cases will give a large or even the dominant part of the interaction free energy for shorter separations too.

To summarize, we have seen how the screened electrostatic interaction,  $w^{\text{el}}$ , can be expressed in the general exact case for electrolyte systems with molecular solvent in a way that is quite similar to how it is done in the PB approximation, but where *all* molecules are treated on the same basis. In the free energy of interaction there is, apart from  $w^{\text{el}}$ , one part,  $w^{\text{dress}}$ , that contains non-electrostatic and indirect electrostatic effects from interactions between the molecular dresses and one part,  $w^{\text{bridge}}$ , that contains more short-ranged contributions from complicated effects of many-body correlations. In many important cases  $w^{\text{el}}$  dominates for intermediate to large separations, for example when the electrolyte concentration is not too high. It is, however, possible for  $w^{\text{dress}}$  to be more long-ranged than  $w^{\text{el}}$ . This happens, for example, at high electrolyte concentration, where the screening decay length is small, and close to a critical point.

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### Appendix

In this appendix we will give a brief exposition of the basic theory for the interaction free energy (potential of mean force)  $w_{ij}(r_{12})$  between two particles of species  $i$  and  $j$  at separation  $r_{12}$  in a fluid. For simplicity in notation we will restrict ourselves to primitive model electrolytes, but the theory for electrolytes with molecular solvent is very similar.

The interaction free energy  $w_{ij}(r_{12})$  is the change in free energy that arises when the two particles are brought from a large separation (in principle an infinite separation) to a distance

$r_{12}$  from each other. It is the sum of the direct pair interaction potential  $u_{ij}(r_{12})$  of the two particles and an indirect contribution  $w_{ij}^{\text{ind}}(r_{12})$  from the interactions with the other particles of the fluid. The latter contribution arises because the particle distribution around the two particles depends on the separation  $r_{12}$  between them.

Instead of calculating the free energy change  $w_{ij}(r_{12})$  when the two particles are brought together, one can obtain the same result by making insertions of one of the particles into the system to two different points:

- (i) to a point in the fluid far away from the other particle and
- (ii) to a point at distance  $r_{12}$  from the other.

One then obtains  $w_{ij}(r_{12})$  by taking the difference between the free energies of insertion for the cases (i) and (ii) (free energy of insertion = reversible work against intermolecular interactions when inserting a particle from outside the system, where it initially does not interact with the molecules in the system). In case (i) the density of the fluid where the particle is inserted is the bulk density. In case (ii) the density at the point of insertion  $\mathbf{r}_1$  is affected by the interactions with the second particle which is located at  $\mathbf{r}_2$  (this density is given by the pair distribution of particles around the second particle).

The quantities that tell how much a difference in density affects the free energy of insertion are called direct correlation functions,  $\mathcal{C}$  (for convenience we will use the notation  $\mathcal{C}$  to denote  $-k_{\text{B}}Tc$ , where  $c$  is the usual direct correlation function in liquid state theory) [12]. The free energy of insertion is influenced by the density distribution in a whole neighbourhood of the insertion point  $\mathbf{r}_1$ . If the contribution from each point  $\mathbf{r}_3$  in this neighbourhood is assumed to be independent of the contributions from the other points, the free energy of insertion is obtained by application of a two-point direct correlation function,  $\mathcal{C}^{(2)}(\mathbf{r}_1, \mathbf{r}_3)$ . (Like all pair functions in bulk  $\mathcal{C}^{(2)}$  only depends on the distance  $r_{13} = |\mathbf{r}_3 - \mathbf{r}_1|$ .) This function tells how much a difference in density at  $\mathbf{r}_3$  influences the free energy of insertion at  $\mathbf{r}_1$  and we have to sum the contributions from all points  $\mathbf{r}_3$ . The contribution to  $w_{ij}^{\text{ind}}(r_{12})$  from, say, the particles of species  $l$  is accordingly

$$\int d\mathbf{r}_3 \mathcal{C}_{il}^{(2)}(r_{13}) [n_l g_{lj}(r_{32}) - n_l],$$

where the square bracket is the difference in density for insertions in case (ii) and (i) respectively. This is an approximation since the contributions from the different points  $\mathbf{r}_3$  are not independent and is called the *hypernetted chain (HNC) approximation*

$$w_{ij}^{\text{HNC}}(r_{12}) = u_{ij}(r_{12}) + \sum_l \int d\mathbf{r}_3 \mathcal{C}_{il}^{(2)}(r_{13}) n_l h_{lj}(r_{32}) \quad (21)$$

where  $h_{lj} = g_{lj} - 1$ . It is often a very good approximation for electrolytes in the primitive model. The dominating contribution to  $\mathcal{C}_{il}^{(2)}(r_{13})$  for large  $r_{13}$  is the electrostatic interaction,  $q_i q_l \phi_{\text{Coul}}(r_{13})$ , but this is not the only contribution. The remaining part of  $\mathcal{C}_{il}^{(2)}$  is a short-ranged contribution that we denote  $\mathcal{C}_{il}^0$  and we have

$$\mathcal{C}_{il}^{(2)}(r_{13}) = q_i q_l \phi_{\text{Coul}}(r_{13}) + \mathcal{C}_{il}^0(r_{13}). \quad (22)$$

(Incidentally, note that if one neglects  $\mathcal{C}_{il}^0$  and replaces  $\mathcal{C}_{il}^{(2)}$  by  $q_i q_l \phi_{\text{Coul}}$  in equation (21) the rhs of this equation turns into  $w_{ij}^{\text{PB}}(r_{12})$ .) According to the Ornstein–Zernike (OZ) equation [10] the last term (the sum) in equation (21) is equal to  $\mathcal{C}_{ij}^{(2)}(r_{12}) - k_{\text{B}}T h_{ij}(r_{12})$ , which makes the HNC approximation for  $w_{ij}(r_{12})$  take on a more familiar appearance.

In the exact case one has to consider the fact that the contributions from the different points in the neighbourhood of the insertion point are not independent. The correction to the

free energy from the interdependence of contributions from two points  $\mathbf{r}_3$  and  $\mathbf{r}_4$  is given by a very similar application of a three-point direct correlation function,  $\mathcal{C}^{(3)}(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_4)$ . We then have the correction to be added to equation (21)

$$\frac{1}{2} \sum_{lm} \int d\mathbf{r}_3 d\mathbf{r}_4 \mathcal{C}_{ilm}^{(3)}(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_4) n_l h_{lj}(r_{32}) n_m h_{mj}(r_{42}),$$

where the factor  $1/2$  appears to avoid double counting. Furthermore, the corrections from the interdependence of contributions from three points is given by a function  $\mathcal{C}^{(4)}$  etc all the way till an infinite number of points. The sum of all these corrections, which we will denote  $w_{ij}^{\text{bridge}}(r_{12})$ , must be added to the rhs of equation (21) to give the exact  $w_{ij}(r_{12})$ , i.e.

$$w_{ij}(r_{12}) = u_{ij}^{\text{short}}(r_{12}) + q_i q_j \phi_{\text{Coul}}(r_{12}) + \sum_l \int d\mathbf{r}_3 \mathcal{C}_{il}^{(2)}(r_{13}) n_l h_{lj}(r_{32}) + w_{ij}^{\text{bridge}}(r_{12}), \quad (23)$$

where we have written the pair potential as  $u_{ij} = u_{ij}^{\text{short}} + q_i q_j \phi_{\text{Coul}}$ . (In more common terminology, the function  $-w_{ij}^{\text{bridge}}(r_{12})/(k_B T) = d(r_{12})$  is called the bridge function, the sum of all ‘bridge diagrams’ [10].) The function  $w_{ij}^{\text{bridge}}(r_{12})$  is in general difficult to evaluate and one often makes some approximation for it. The HNC approximation is to set it equal to zero.

It now remains to identify  $w_{ij}^{\text{el}}$  and  $w_{ij}^{\text{dress}}$  in the rhs of equation (23). From the anticipated result  $w_{ij} = u_{ij}^{\text{short}} + w_{ij}^{\text{el}} + w_{ij}^{\text{dress}} + w_{ij}^{\text{bridge}}$  we see that they must originate from the two middle terms in equation (23). The term  $q_i q_j \phi_{\text{Coul}}$  contributes to  $w_{ij}^{\text{el}}$  while the third term (the sum) in equation (23) contains  $w_{ij}^{\text{dress}}$  and the rest of  $w_{ij}^{\text{el}}$ . We will only give a brief outline of how these identifications can be made. Firstly, one uses the OZ equation to write  $h_{lj}$  as an infinite sum of terms involving  $\mathcal{C}^{(2)}$  functions only (the terms are integrals of products, so-called chains, of  $\mathcal{C}^{(2)}$  functions). The third term in equation (23) then becomes expressed solely in  $\mathcal{C}^{(2)}$  functions. Secondly, one uses equation (22) to replace every one of these  $\mathcal{C}^{(2)}$  functions by the sum of  $\mathcal{C}^0$  and the Coulombic pair potential. One can now separate the resulting terms into two groups, one with the terms that only contain  $\mathcal{C}^0$  functions (but no  $\phi_{\text{Coul}}$ ) and one with the remaining terms (it has terms that contain only  $\phi_{\text{Coul}}$  functions or both  $\phi_{\text{Coul}}$  and  $\mathcal{C}^0$  functions). The sum of the terms in the former group constitutes  $w_{ij}^{\text{dress}}$ , and one can show that the sum of the latter, together with  $q_i q_j \phi_{\text{Coul}}$  in equation (23), is equal to  $w_{ij}^{\text{el}}(r_{12})$  defined in equation (15).

The function  $w_{ij}^{\text{dress}}$  involves non-electrostatic and indirect electrostatic effects from interactions between ionic dresses. In fact,  $w_{ij}^{\text{dress}}$  can be written like the third term in equation (23), but with  $\mathcal{C}_{il}^0$  and distribution functions,  $h_{lj}^0$ , of the ionic dresses instead of the full distribution functions. The functions  $h_{lj}^0$  are related to  $\mathcal{C}_{ij}^0$  via the OZ equation, see [3, 9], and constitute the distribution functions that give the dressed ion charge distribution  $\rho_i^0$ .

The final result is that equation (23) can be written as

$$w_{ij} = u_{ij}^{\text{short}} + w_{ij}^{\text{el}} + w_{ij}^{\text{dress}} + w_{ij}^{\text{bridge}} \quad (24)$$

which is the complete, exact expression for  $w_{ij}$ .

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