

A Simple Correlation-Corrected Poisson–Boltzmann Theory

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Received: January 30, 2004; In Final Form: March 30, 2004

A simple approach is used to introduce effects of ion–ion correlations into the Poisson–Boltzmann theory. The mean-field character of the theory is retained and correlations are approximated by an effective interaction potential, which differs from the Coulombic at short range. In particular, the severe overestimation of the average interaction energy between ions of like charge inherent in the original Poisson–Boltzmann theory, is accounted for by this effective potential. We show that important phenomena due to ion–ion correlations, such as net attraction between surfaces of like charge and charge reversal in double layer systems, are qualitatively and semiquantitatively reproduced by this correlation-corrected theory, which contains no adjustable parameter. The response of net surface interactions to the addition of salt is also captured by the theory and satisfactory quantitative agreement is found with simulation results, even at molar concentrations of divalent salt and in the presence of highly charged surfaces. The mean-field theory is furthermore able to qualitatively predict the way in which bulk salt properties such as the osmotic coefficient and the excess chemical potential depend on the salt concentration. The quantitative performance is poorer than for electric double layer systems, but there is still a substantial improvement relative to the ordinary Poisson–Boltzmann theory.

1. Introduction

Interactions between charged surfaces are of seminal importance in colloidal science and in virtually all biological systems. Hence, such interactions have been extensively studied for many decades, with the DLVO theory^{1,2} as the fundamental reference. One of the simplest and most common approaches is to adopt a dielectric continuum description of the solvent (the primitive model) and use the Poisson–Boltzmann (PB) theory to predict ion distributions and surface interactions. The major virtues of PB calculations is that they run very fast and the theory is simple and thermodynamically consistent in the sense that sum rules, such as the contact theorem,³ are fulfilled. It is furthermore reasonably accurate for weakly coupled systems and provides correct limiting behaviors, such as the decay of the force between charged surfaces at large separations.⁴ The major drawback is the inability of the theory to predict attraction between surfaces of equal charge, even qualitatively.⁵ Such attractions, the origin of which are *ion–ion correlations*, have been the focus in a considerable number of studies in recent years. Correlation attractions in ionic solutions were first proposed by Oosawa,⁶ and these predictions were later qualitatively verified by integral equation calculations^{7,8} and simulations⁹ of strongly coupled primitive model systems. Attractions due to ion–ion correlations, which are primarily observed in multivalent systems, have been suggested as an important mechanism in a diverse range of phenomena, such as phase equilibria between liquid crystalline phases,^{10,11} DNA folding,¹² and the onset of cohesion in cement.¹³ A thorough review on ion–ion correlations and their consequences is given in ref 14.

In this article, we make an attempt to remedy the major weakness of the PB theory, i.e., its inability to describe effects due to ion–ion correlations, while retaining its simplicity. Hence, we will keep the mean-field character of the theory and introduce correlations in an *effective* way, by modifying the interaction potential in the range where correlations are impor-

tant. In particular, the average interaction energy between ions of like charge is overestimated in the original PB theory, because it does not take into account that configurations in which the ions are closely separated, rarely occur. The most common way to deal with this problem is to introduce approximations for the radial distributions functions. This is the integral equation approach, which can lead to accurate predictions, at the expense of a considerable increase in algebraic complexity and computational effort. The flaw of the PB can, however, in principle be corrected by the use of an effective potential, which is less repulsive than the pure Coulomb interaction in a region where correlations are important. This is the approach we shall pursue in this work. We will show that the resulting theory, which will henceforth be denoted cPB, is able to qualitatively, and even semiquantitatively, predict attractive double layer interactions in strongly coupled systems. Related phenomena, such as charge reversal and effects of increased salt concentration, are also reproduced by the cPB theory. Even bulk properties, such as the variation of the activity coefficient and osmotic coefficient with salt concentration, are qualitatively reproduced by the mean-field theory, although the quantitative agreement is less satisfactory. The improvement is nevertheless dramatic compared with the original theory, which predicts constant values of these properties regardless of valencies and salt concentration. Physically reasonable behavior will in that case be obtained, at low salt concentrations, if we resort to the Debye–Hückel approximations, where correlations are “built in” in the usual way via the screening length. The quantitative performance of that theory is poor, except at low salt concentrations, where the deviation from ideal behavior is small anyway.

There are of course other successful theories of ionic solutions, such as HNC and its anisotropic extensions,^{7,15–17} the modified Poisson–Boltzmann theory,^{18–20} the dressed ion theory,^{21–23} the hole corrected Debye–Hückel theory,^{24–28} the generalized van der Waals theory,^{29–32} and the strong coupling

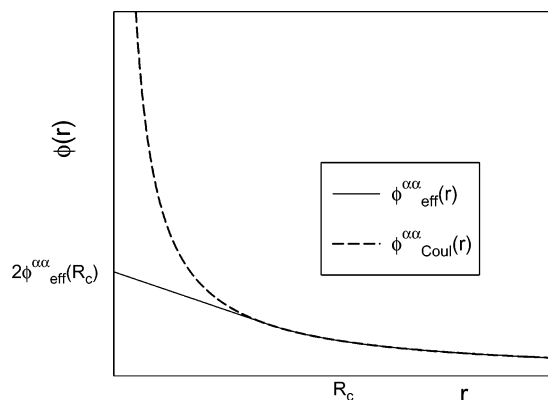


Figure 1. Illustration of the effective potential, $\phi_{\text{eff}}^{\alpha\alpha}$, used in the cPB theory.

theory.^{4,33} These theories are often more accurate than the cPB, for the systems they are constructed to describe. However, this is in many cases only a subset of the range of systems that can be incorporated by the cPB formalism. For example, the hole corrected Debye–Hückel theory can predict properties of bulk salt solutions with high accuracy, but it is not clear if and how a Debye–Hückel type of theory could be applied to highly anisotropic systems, such as the electric double layer in slit geometries or in the absence of salt. The generalized van der Waals theory reduces (at least in its simpler forms) to the Poisson–Boltzmann theory in the case of dissolved point charges that neutralize charged surfaces. Such salt-free systems will display attractive surface forces, provided the coupling strength is sufficiently high.⁹ The strong coupling theory is, as the name suggests, only applicable to systems in which the electrostatic coupling is exceptionally high.

The cPB, on the other hand, is at least in principle applicable to bulk salt solutions as well as electric double layer systems, at high or low coupling strengths, and with or without added salt. All the alternative theories mentioned are furthermore more complex than the cPB and an important advantage of the cPB, in comparison with these, is that it shares the simplicity of the original PB theory. In fact, expanding an existing PB program to cPB will in general only require a handful of extra lines of code and the new cPB program will run just as fast as its original PB version.

The article is outlined as follows: the cPB theory is described in the next section, which is followed by a presentation of results. These cPB results are compared with predictions by simulations or alternative theories. In the last section, we discuss the results and suggest some possibilities for improvements and subsequent research.

2. Theory

We shall start by writing the Poisson–Boltzmann expression in a density functional form, which leads to the following free energy functional, $\mathcal{F}[n_{\alpha}(\mathbf{r})]$:

$$\beta \mathcal{F}[n_{\alpha}(\mathbf{r})] = \int \sum_{\alpha} n_{\alpha}(\ln[n_{\alpha}(\mathbf{r})] - 1) d\mathbf{r} + \frac{\beta}{2} \int \int \sum_{\alpha} \sum_{\gamma} n_{\alpha}(\mathbf{r}) n_{\gamma}(\mathbf{r}') \phi_{\text{Coul}}^{\alpha\gamma}(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r} d\mathbf{r}' + \beta \int \sum_{\alpha} V_{\text{ex}}(\mathbf{r}) n_{\alpha}(\mathbf{r}) d\mathbf{r} \quad (1)$$

where β is the inverse thermal energy, n_{α} is the density of ion species α , V_{ex} is an external potential, and $\phi_{\text{Coul}}^{\alpha\gamma}(r)$ is the

Coulomb interaction energy between ions α and λ , separated a distance r :

$$\beta \phi_{\text{Coul}}^{\alpha\lambda}(r) = l_{\text{B}} \frac{z_{\alpha} z_{\lambda}}{r} \quad (2)$$

The valency of ion α is denoted by z_{α} , and $l_{\text{B}} = \beta e^2 / (4\pi\epsilon_0\epsilon_r)$ is the Bjerrum length. The elementary charge is denoted by e , and ϵ_0 and ϵ_r are the permittivity of vacuum and the dielectric constant of the (continuum) solvent, respectively.

As mentioned previously, we aim to introduce correlations in an effective way, by reducing the mean-field repulsion between ions of like charge when the separation between them is smaller than some value R_c^{α} :

$$\phi_{\text{eff}}^{\alpha\alpha}(r) = \begin{cases} \phi_{\text{Coul}}^{\alpha\alpha}(r) & r > R_c^{\alpha} \\ \phi_{\text{corr}}^{\alpha\alpha}(r) & r \leq R_c^{\alpha} \end{cases} \quad (3)$$

where $\phi_{\text{corr}}^{\alpha\alpha}(r) < \phi_{\text{Coul}}^{\alpha\alpha}(r)$. We have not yet specified how to calculate R_c^{α} , but it is clear that it should be related to the average separation between neighboring α -ions in the solution. As for $\phi_{\text{corr}}^{\alpha\alpha}$, we suggest the following ad hoc choice:

$$\phi_{\text{corr}}^{\alpha\alpha}(r) = \left(\frac{d\phi_{\text{Coul}}^{\alpha\alpha}}{dr'} \right)_{r'=R_c^{\alpha}} (r - R_c^{\alpha}) + \phi_{\text{Coul}}^{\alpha\alpha}(R_c^{\alpha}) \quad (4)$$

There are several other alternatives, which in principle also will improve the original theory. This particular choice has some extra physical appeal because ϕ_{eff} , as well as its derivative, is continuous at the transition distance R_c . Another motivation is the way in which it leads to satisfactory predictions of various properties under very different circumstances. This will be demonstrated in the next section. The difference between $\phi_{\text{eff}}^{\alpha\alpha}$ and the pure Coulombic interaction is illustrated in Figure 1.

In the slit geometries we shall be interested in, we can integrate in the direction (y, z) parallel with the charged surfaces, to obtain

$$\beta \phi_{\text{eff}}^{\alpha\alpha}(|x|) = \begin{cases} -2\pi z_{\alpha}^2 l_{\text{B}} |x| & |x| > R_c^{\alpha} \\ \frac{2\pi z_{\alpha}^2 l_{\text{B}}}{R_c^{\alpha}} \left(\frac{|x|^3}{3R_c^{\alpha}} - \frac{(R_c^{\alpha})^2}{3} - |x|^2 \right) & |x| \leq R_c^{\alpha} \end{cases} \quad (5)$$

where the x direction is normal to the surfaces.

In simulations of solutions containing both negatively and positively charged ions, the attractive divergence of the Coulomb interaction has to be dealt with, either via some truncation or by including a model of the Pauli repulsion between these species. A common approach is to add a hard sphere exclusion interaction. Sometimes such an interaction is also added between ions of like charge, but unless the concentration is very high, or the hard sphere diameter is very large, this has virtually no influence on the properties of the system. It should be emphasized that *the primitive model is unsuited for evaluations of hard core effects*. The reason is that the solvent particles, which naturally will dominate the excluded volume properties of the system, are treated as a continuum. It may be possible to capture relevant excluded volume effects between positive and negative ions, because these attract each other strongly. However, if a primitive model reveals significant hard core effects due to exchange repulsions between ions of like charge, there is reason to be very careful with the interpretation of this result. It actually indicates that the primitive model may be inadequate for that particular system. This problem has been highlighted

in simulations and density functional calculations of double layer systems.^{32,34–36} Similar predictions were obtained with an extended version of the modified Poisson–Boltzmann theory.²⁰ The results obtained from these and other^{16,37–39} studies strongly suggest that to obtain a reasonably accurate estimate of hard core effects, the solvent *has to be* taken into account. Such effects are expected to be of particular importance in systems containing large ions, in which case there will be solvent-induced depletion forces acting between the ions and at surfaces.^{40–46} In systems where there are a number of ions with different sizes, we anticipate more complex solvent-induced effects. There has been some interesting attempts to do this in a simplistic manner, e.g., via a lattice model, employing a net incompressibility constraint,^{47,48} or via an approximate solvent-mediated potential of mean force.^{49,50} Unfortunately, the approximations inherent in these approaches are likely to be poorer for size-asymmetric systems, where solvent hard core effects are particularly important. More accurate (and more complex) methods, such as integral equation^{16,37} and density functional^{35,36} theories, or the modified Poisson–Boltzmann approach^{20,51} are viable alternatives for size-asymmetric systems at the solvent primitive model level.

At any rate, because we are working with a simple version of the PB theory for *restricted primitive model* systems, where the solvent is treated as a continuum, we have no desire to include excluded volume effects due to hard core repulsions. Instead, the primary effect of the Pauli repulsion between positively and negatively charged ions is modeled by a *loss of attraction* as the separation is less than the “hard sphere diameter”:

$$\phi^{\alpha\lambda}(r) = \begin{cases} \phi_{\text{Coul}}^{\alpha\lambda}(r) & r > d_{+-} \\ 0 & r \leq d_{+-} \end{cases} \quad (6)$$

where α and λ have valencies of opposite sign. In a slit geometry, this leads to

$$\beta\phi^{\alpha\lambda}(|x|) = \begin{cases} -2\pi z_{\alpha} z_{\gamma} l_B |x| & |x| > d_{+-} \\ -2\pi z_{\alpha} z_{\gamma} l_B d_{+-} & |x| \leq d_{+-} \end{cases} \quad (7)$$

Given the approximations inherent in the primitive model, we think that a preferable way to simulate ionic solutions would be to exclude hard core interactions between like charged species and merely truncate the interaction below some separation d_{+-} , between ions of opposite charge. This would be consistent with the level of approximation and also with the way in which we partition the interactions in the cPB theory. Furthermore, this “loss of attraction approach” will give results that are identical to those obtained in the presence of hard cores, with the exception of systems containing large and very weakly charged macroions. In other words, even though the former approach in principle allows ions of opposite charge to pile on top of each other, the energy cost is generally high enough to render such configurations extremely unlikely, and of no thermodynamic significance.

Let us proceed with the determination of the transition distance R_c . As mentioned earlier, it should reflect the average nearest-neighbor distance between ions of like charge. In systems containing charged surfaces, the mean distance between neighboring counterions will be relatively small near the surfaces (unless the surface charge density is very low, a limit that will be discussed separately below). Far away from the surfaces, this separation will on average be larger. This suggests the use of an anisotropic treatment of $\phi_{\alpha\alpha}$, i.e., with different R_c^{α} 's in the direction parallel with and transverse to the surfaces,

respectively. However, in this initial study, we have chosen the more simplistic “spherical” approach, with a single transition distance:

$$R_c^{\alpha} = \sqrt{\frac{e}{\pi} \frac{|z_{\alpha}|}{\sigma}} \quad (8)$$

If ion α is a counterion to the surface, R_c^{α} is defined from the area per ion when the counterions are condensed at the surface to the extent that they exactly neutralize the surface charge. If we let this area per ion be circular, R_c^{α} is the radius of that circle. To obtain consistency, the transition distance between coions is also defined by eq 8. In essence, the transition distance is determined by the proximity between counterions near the charged surface, where the density is highest and correlation effects are most important. As we shall see, this choice can be further motivated by good agreement with simulated results, even for highly coupled systems.

There are of course alternative possibilities. We could, for instance, use a more drastic approach in which the effective potential drops to zero below some hard core distance, which in essence would define a “Coulomb hole”. We have tried such schemes, including free energy minimizations along the lines previously used for the generalized van der Waals theory of Lennard-Jones fluids.⁵² However, this approach is more complex and is, for the systems studied here, still ambiguous in terms of the densities and locations at which to perform the minimization. Furthermore, such methods are more consistent with density functional approaches, containing some estimate of excluded volume contributions to the entropy. One would also on physical grounds expect a “gradual Coulomb hole” to be a better estimate of ion–ion anticorrelations effects. This is confirmed by the fact that the results we have obtained by these alternative methods have at best been comparable to those obtained with the suggested, more simplistic, approach.

Obviously, another choice has to be made for R_c^{α} in systems that do not contain charged surfaces, i.e., bulk salt solutions. We postpone a discussion on bulk salt solutions and assume, for the time being, that the systems we are interested in do contain charged surfaces.

We emphasize that the precise way in which the true Coulombic interaction is replaced by a less repulsive effective potential at short range is not crucial for the qualitative improvement of the theory. In fact, including a simple “Coulomb hole”, as mentioned above, is enough to obtain qualitatively correct results, even without excluded volume contributions to the entropy. This is most likely one of the main reasons why density functional theories of ionic solutions are so successful. In other words, their ability to treat excluded volume effects is of secondary importance, unless of course the solvent is included *explicitly*.³⁵ Instead, correlation attractions in primitive model systems, which are so well reproduced by density functional theories, are primarily related to the reduced mean-field repulsion between ions of like charge that results from the presence of hard spheres.

Note that the structure of the free energy functional, eq 1, is still the same, and the only change that has to be made in an existing PB program is the mean-field potential. This will normally require just a few extra lines of code and there is no extra computational cost.

3. Results

3.1. Electric Double Layer Systems. We shall start by considering double layer systems, i.e., two charged and opposing

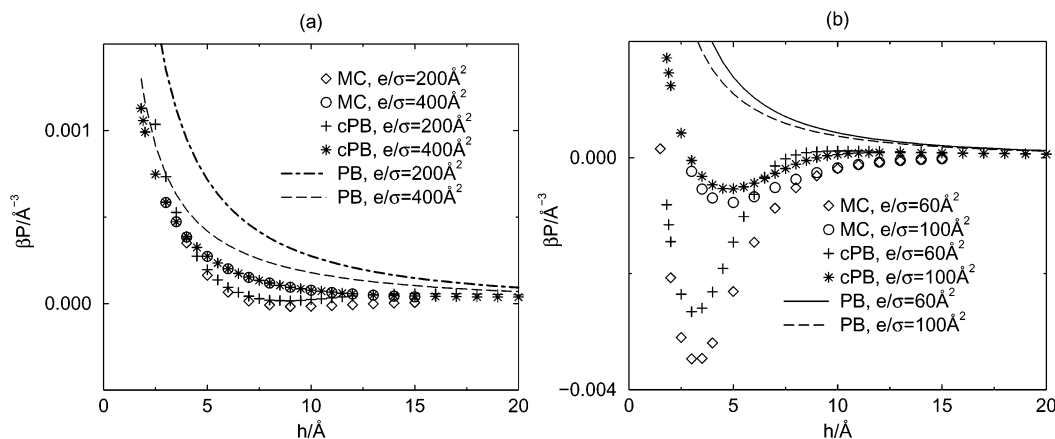


Figure 2. Predictions of the osmotic pressure in a double layer system with pointlike divalent counterions, no salt, and surfaces with various charge densities

planar surfaces, between which an electrolyte is confined in a primitive model system. In general, this electrolyte is in equilibrium with a bulk salt solution, although we will also investigate the special case where the solution only contains neutralizing counterions. The continuum solvent has a dielectric constant $\epsilon_r = 78.3$, and the temperature is 298 K. The walls have a uniform surface charge density σ and are separated a distance h . The slit geometry allows analytic integration of $\mathcal{A}[n_\alpha(\mathbf{r})]$ in the (y, z) direction parallel with the surfaces, to obtain $\mathcal{A}[n_\alpha(x)]$. The grand potential, Ω , for the system is then generated from a Legendre transformation:

$$\beta\Omega = \beta\mathcal{F} + 2\pi l_B \sigma^2 h / e^2 - \sum_\alpha \mu_\alpha \int_0^h n_\alpha(x') dx' \quad (9)$$

where μ_α is the chemical potential of ion α . Minimizing the grand potential leads to the following integral equation for the ionic densities in the slit:

$$n_\alpha(x) = \exp[2\pi\sigma l_B h z_\alpha + \beta(\mu_\alpha + z_\alpha \Psi_D - \sum_\lambda \int_0^h n_\lambda(x') \phi_{\text{eff}}^{\alpha\lambda}(|x-x'|) dx')] \quad (10)$$

which can be solved by various methods, the simplest of which is iteratively, via Picard iterations where a portion of the “old” solution ($n(x)$ in RHS) is mixed with the “new” ($n(x)$ in LHS) one, to ensure stable convergence.⁵³ Electroneutrality is maintained by a Donnan potential, Ψ_D . Note that the interaction potentials, $\phi_{\text{eff}}^{\alpha\lambda}(|x|)$, only have to be calculated once, with the results in each case stored in a vector. It is then clear that transforming the calculation program from cPB to PB, or vice versa, essentially amounts to an interchange between $\phi_{\text{eff}}^{\alpha\lambda}(|x|)$ and $\phi_{\text{Coul}}^{\alpha\lambda}(|x|)$ in the loop where these vector elements are calculated. There is also a slight change in the expressions for the bulk chemical potentials, as will be described in the next section. It is obvious that cPB calculations will run as fast as corresponding ones with PB.

Initially, we will consider cases where the charged surfaces are neutralized by counterions only, i.e., the salt-free case. Results for divalent counterions and various surface charge densities are displayed in Figure 2. Contrary to the original PB theory, cPB predicts results that are qualitatively and even semiquantitatively in agreement with those from Metropolis Monte Carlo simulations (MC). These simulations were performed in a standard manner and followed the recipe outlined in ref 9. Given the crudeness of the primitive model, the

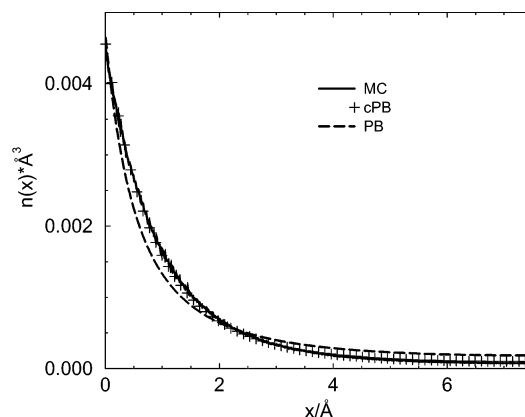


Figure 3. Predictions of the counterion density in a primitive model double layer system in the salt-free case, with pointlike divalent counterions. The surface charge density is given by $e/\sigma = 60 \text{ \AA}^2$, and the two surfaces are 15 \AA apart.

quantitative agreement is quite satisfactory, even for highly charged surfaces.

The density distributions also display a nearly quantitative agreement with simulated data, as can be seen in Figure 3. It is interesting that we observe such a structural agreement in this highly anisotropic system. The PB formulation, in its simplest version, is particularly well suited for descriptions of such systems. This is of course the reason the Guy-Chapman theory is so popular and commonly used in descriptions of such systems. The cPB shares this property and we shall demonstrate that although it, contrary to PB, can be applied as a rough guide to bulk solution properties, its performance in highly anisotropic systems is indeed more satisfactory. This will be further discussed in the next section.

Predicted surface interactions in corresponding systems with monovalent counterions are presented in Figure 4. Again, the quantitative agreement between cPB theory and simulations is excellent, with some significant deviations at the highest surface density in a region above 4 \AA . The reason for this discrepancy is probably that the electrostatic coupling strength is almost strong enough for an oscillation in the pressure curve to build up. This has been corroborated (not shown) by calculations and simulations with exceptionally high surface charge densities.

Trivalent counterions naturally lead to very strongly coupled systems, but the cPB still produces relatively accurate predictions, as demonstrated in Figure 5. The ability to successfully describe systems with such a vast difference in coupling strength (cf. Figure 4), is of course a very appealing property of the cPB.

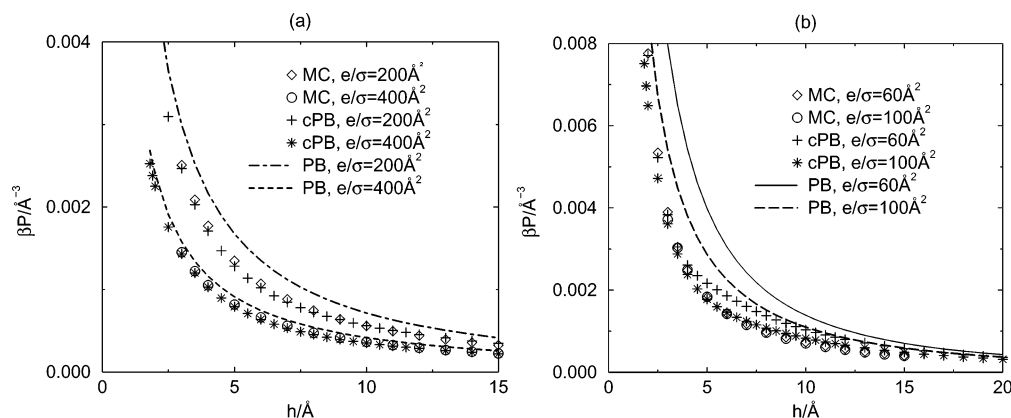


Figure 4. Predictions of the osmotic pressure in a primitive model double layer system with pointlike monovalent counterions, no salt, and surfaces with various charge densities.

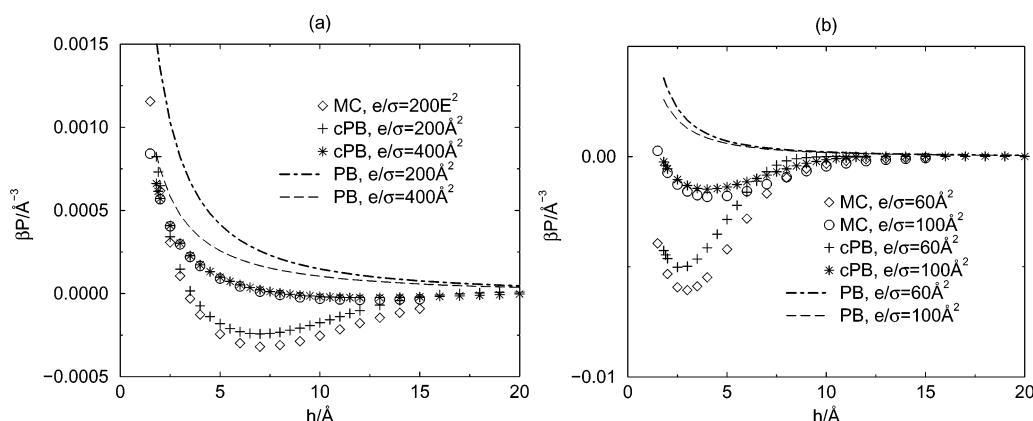


Figure 5. Predictions of the osmotic pressure in a primitive model double layer system with pointlike trivalent counterions, no salt, and surfaces with various charge densities.

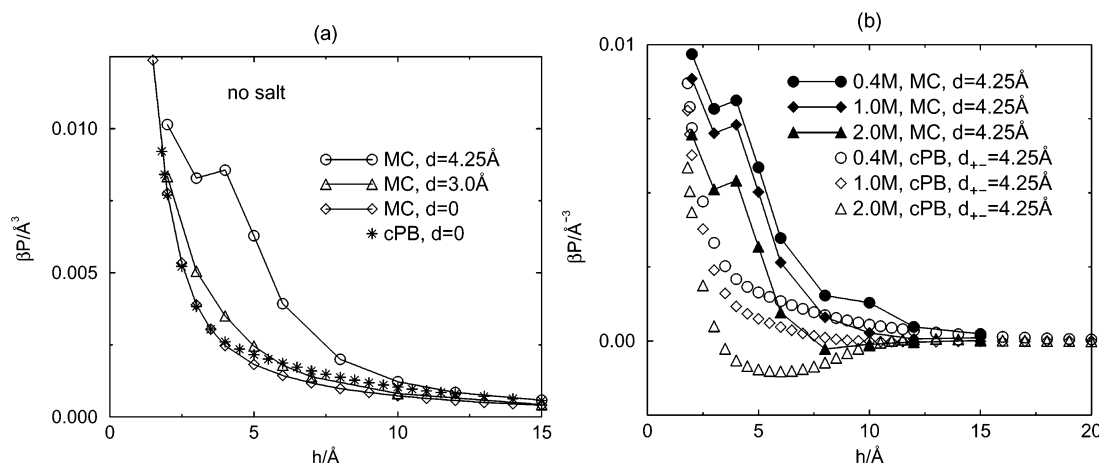


Figure 6. Predictions of the net osmotic pressure in a double layer primitive model system immersed in a 1:1 salt solution. The surface charge density is given by $e/\sigma = 60 \text{ Å}^{-2}$. In the simulations,⁵⁴ there is a hard sphere interaction, with diameter d , between all ions. In the cPB, hard core effects only enters as a loss of interaction between ions of like charge, when the separation between them is less than $d_{+-} = d$. Hence, hard core exclusion between ions of like charge is not included by the cPB. The effect of such hard core interactions in the simulation model, is demonstrated in (a), where the salt concentration is zero. (b) shows predictions for $d = 4.25 \text{ Å}$, at different bulk salt concentrations.

We shall next investigate surface interactions when the charged walls are immersed in an electrolyte solution with a finite salt concentration. We compare the cPB predictions with results from simulations, as obtained in a study by Åkesson and Jönsson.⁵⁴ A slight complication is that they used a large hard sphere diameter, $d = 4.25 \text{ Å}$ between all species. This leads to noticeable packing effects, even between ions of like charge, as shown in Figure 6a. We see that the pressure oscillation observed at short separations vanishes if the hard sphere diameter is small enough. As we mentioned earlier, the

primitive model cannot really be expected to produce reasonable estimates of such packing effects and they are not incorporated into the cPB formalism. The difference in the way by which hard sphere effects are treated in the simulations and in the cPB theory, respectively, makes comparisons between the two less straightforward. As we shall see, these problems essentially disappear when the counterions are multivalent. Nevertheless, even for monovalent counterions (1:1 salt), we should be able to compare the qualitative response of the surface forces, to addition of salt. Such a comparison has been made in Figure

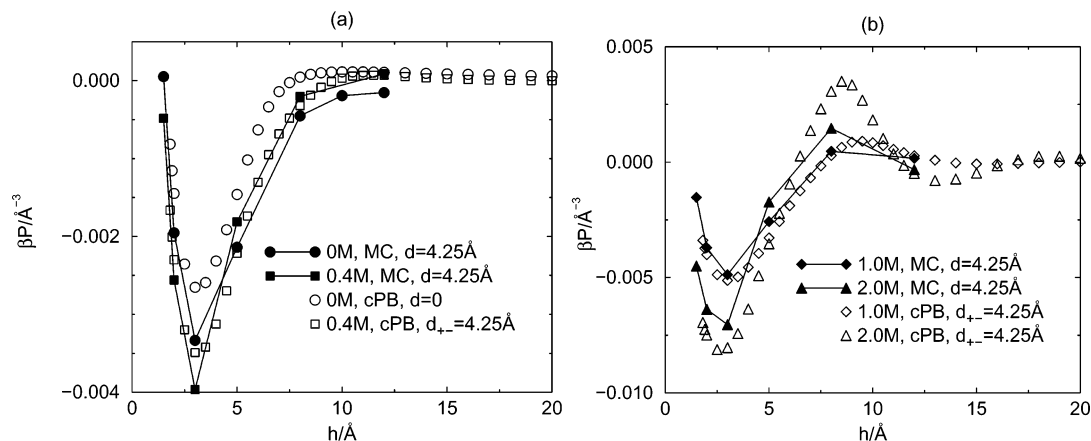


Figure 7. Predictions of the net osmotic pressure in a double layer system immersed in a 2:1 salt solution, where the divalent species is counterion to the charged surfaces. The surface charge density is given by $e/\sigma = 60 \text{\AA}^2$ and $d = 4.25 \text{\AA}$. MC simulation data from Åkesson et al.⁵⁴

6b. We observe the same qualitative trend in both cases, namely that the repulsion decreases as salt is added. At high salt concentrations, there is even an attractive regime.

Let us proceed to the case of a 2:1 salt solution, where the divalent species is counterion to the surfaces. The results are displayed in Figure 7, for various salt concentrations. The quantitative agreement is surprisingly good, with substantial deviations occurring only for very high salt concentrations. We have demonstrated that hard core interactions between ions of like charge can give substantial contributions to the net pressure curve in 1:1 solutions, if the hard sphere diameter is as large as 4.25\AA . In this case, however, such effects are insignificant, due to the strong anticorrelation between divalent counterions. Note that the oscillations appearing in the pressure curve at high salt concentrations is actually exaggerated by cPB, despite the fact that it does not include any Pauli (hard sphere) repulsions. In the cPB, these oscillations are due to the loss of attractive interactions, brought about by the “excluded attraction hole” (d_{+-}), as the ions pack in the slit. This again indicates that the success of density functional theories for double layer systems is primarily related to the inclusion of “excluded attraction holes” ($+-$), as well as “anticorrelation holes” ($++$, $--$), rather than to their ability to model hard core effects. It should be mentioned, though, that an explicit solvent model easily can be incorporated within the generalized van der Waals formalism (at least as hard spheres),³⁵ which enables the study of forces between charged surfaces with more realistic model systems than can be treated by cPB or is manageable simulations.

Another interesting phenomena that these systems are known to display is “charge reversal”;^{16,55} i.e., counterions crowd at a charged surface to such an extent that they overcompensate the net charge of the surface. This generates an “apparent surface charge density”, σ_{app} , of opposite sign. σ_{app} is defined as

$$\sigma_{\text{app}}(x) = \sigma + \int_0^x \sum_{\alpha} n_{\alpha}(x') z_{\alpha} dx' \quad (11)$$

where the sum includes all ionic species. The cPB is able to reproduce charge reversal almost quantitatively, at least in the case illustrated in Figure 8. Note that the phenomenon can be interpreted as a purely electrostatic effect; i.e., it does not appear to be strongly related to hard core correlations in the primitive model. A similar conclusion was drawn in a previous study by Sjöström et al.⁵⁷ In a model system with explicit solvent representation, one may possibly observe an oscillatory behavior of the apparent surface charge (i.e., repeated charge inversions).³²

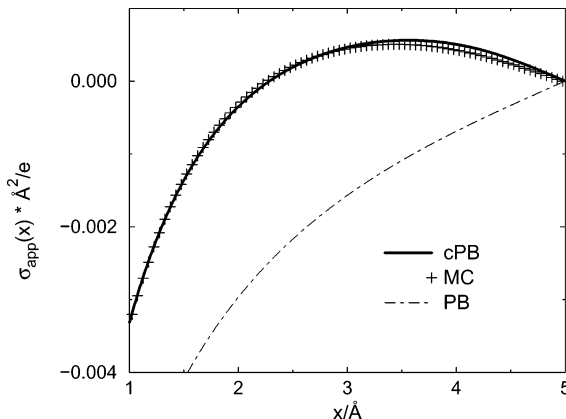


Figure 8. Variation of the apparent surface charge density as a function of the distance (x) from a surface with a uniform surface charge density σ , where $e/\sigma = 60 \text{\AA}^2$. The counterions are divalent and the average 2:1 salt concentration in the slit is 0.3 mol L^{-1} . The separation is $h = 10 \text{\AA}$. The MC simulation data were provided by Åkesson.⁵⁶

As a final test of the cPB theory on double layer systems, we will compare cPB predictions with simulations and experimental results on a lamellar system, which displays phase separation. In the ternary system NaAOT–water– $\text{Ca}(\text{AOT})_2$ (AOT \equiv bis(2-ethylhexyl)sulfosuccinate), coexistence between two lamellar phases with different repeat distances has been observed experimentally.¹⁰ In the corresponding primitive model system, which was simulated by Turesson et al.,¹¹ the pointlike counterions were neutralizing two planar surfaces, bearing a uniform surface charge density. Obviously, the counterions will distribute nonuniformly between the two separate phases. The phase separation as such is a consequence of the oscillatory behavior of the osmotic pressure curve; i.e., it describes a van der Waals loop and the surface separation in the coexisting phases can be determined by a Maxwell equal area construction. We have carried out cPB calculations on an identical model system, and the resulting phase diagram is compared with the simulated and experimental ones in Figure 9. The agreement between cPB predictions, simulations, and experimental data is surprisingly good, given the degree of complexity of the system, with its possibility of particle exchange between the phases. It should be noted that there is some ambiguity in the way the experimentally measured separations should be mapped to the (well-defined) primitive model separations.¹¹ The quantitative agreement between simulations and theory, which use identical parameters, is nevertheless satisfactory and lends

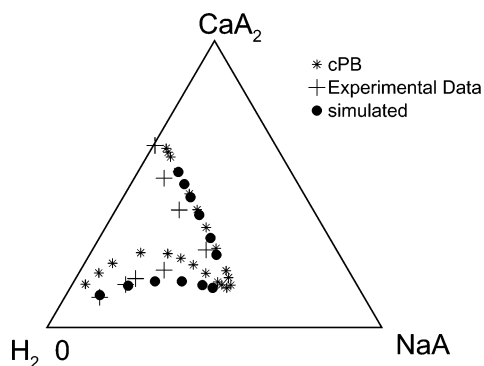


Figure 9. Phase diagram of the NaAOT–water–Ca(AOT)₂ system, as measured experimentally,¹⁰ simulated by a semi-grand canonical scheme¹¹ and calculated by cPB, respectively. The way in which the experimental bilayer system is mapped to the primitive model system is described in detail in ref 11.

further support to the cPB approach. As expected, the ordinary PB theory fails to predict any phase separation at all in these systems.

3.2. Bulk Salt Solutions. We shall now proceed to investigate bulk salt solutions. As mentioned previously, we then need another estimate for R_c^α , because eq 8 is based on the assumption that the systems contain reasonably charged surfaces. We can still adopt the notion that the transition distance should reflect the nearest neighbor distance between ions of like charge. If these ions had been so strongly correlated that they formed a simple cubic lattice, we would have obtained R_c^α from $n_\alpha(R_c^\alpha)^3 = 1$. However, they are not expected to be quite so strongly correlated. A more reasonable estimate is $n_\alpha(R_c^\alpha)^3 = 0.5$, which corresponds to a “reduced density” of 0.5. In a hard sphere system, this would lead to a relatively strongly correlated, but still fluidlike, behavior. We have made some checks with simulations of bulk salt solutions that confirms this is a reasonable, though possibly not optimal, choice. At any rate, we shall demonstrate that it is sufficiently accurate for our purposes in this study, which is to establish the ability of cPB to predict qualitatively correct behavior of salt solutions. Hence, we set

$$R_c^\alpha = \left(\frac{1}{2n_\alpha} \right)^{1/3} \quad (12)$$

Note that the cubic root dependence renders R_c^α relatively insensitive to small changes of our chosen “reduced density”.

There is of course also a regime, in which there is a salt solution, but also weakly charged surfaces, present. In such cases, R_c^α is defined from

$$\min \left(\sqrt{\frac{e|z_\alpha|}{\pi|\sigma|}}, \left(\frac{1}{2n_\alpha} \right)^{1/3} \right)$$

where α is the counterion with the highest valency. The transition distances for the other ions are then determined by the same recipe as for this ion, to avoid inconsistencies. Note that in the previous section, the surface charge density was always high enough for R_c^α to be determined by eq 8.

In our discussion on bulk salt solutions, we will focus on the osmotic coefficient, ϕ , and the mean ionic activity coefficient, γ . We obtain the bulk free energy by integrating the functional, eq 1, with the replacement of $\phi_{\text{Coul}}^{\alpha\lambda}$ by the corresponding cPB potentials, as defined by eqs 3, 6, and 12. By calculating the appropriate derivatives of this free energy, we arrive at the cPB

expressions for the activity coefficient and the osmotic coefficient, respectively. Assuming that the solution contains ionic species α and λ , these expressions read:

$$\phi = 1 + (n_\alpha + n_\lambda)^{-1} \left(\frac{1}{2} e_{\alpha\alpha} n_\alpha^2 + \frac{1}{2} e_{\lambda\lambda} n_\lambda^2 + e_{\alpha\lambda} n_\alpha n_\lambda \right) \quad (13)$$

and

$$\ln \gamma = (|z_\alpha| + |z_\lambda|)^{-1} (|z_\alpha| e_{\alpha\alpha} n_\alpha + |z_\lambda| e_{\lambda\lambda} n_\lambda + e_{\alpha\lambda} (|z_\alpha| n_\lambda + |z_\lambda| n_\alpha)) \quad (14)$$

where

$$e_{\alpha\alpha} = -\frac{z_\alpha^2 \pi l_B}{3} (R_c^\alpha)^2 \quad (15)$$

with an analogous expression for $e_{\lambda\lambda}$ and

$$e_{\alpha\lambda} = 2\pi |z_\alpha z_\lambda| l_B d_{+-}^2 \quad (16)$$

Note that this means that we will try to use a *pure mean-field* theory to describe properties of bulk salt solutions. We should therefore lower our expectations, relative to electric double layer problems, regarding the quantitative performance of the theory. Our main objective is to investigate qualitative behaviors. As usual, there are no hard cores in the cPB treatment but effects of hard core interactions between ions of opposite charge are still taken into account because the attraction is truncated at the hard sphere diameter (it is zero *below* d_{+-}). We shall compare the cPB predictions with experimental data as well as with predictions by the corrected Debye–Hückel theory (CDH),^{29,28} which is a relatively simple, yet successful, theory for bulk salt solutions.

In a recent CDH study, Abbas et al.²⁸ used ionic diameters that were fitted to match experimental data on the corresponding mean activity coefficients. To evaluate the ability of cPB to *predict* values of this quantity, as well as of the osmotic coefficient, we shall instead use an independent source of information: we equate d_{+-} by the average ionic Pauling diameter, as obtained from crystallographic data.

Because our approach contains no adjustable parameter, one would expect poorer performance, at least for the predictions of mean activity coefficients. Indeed, the cPB predictions for this quantity are quantitatively poor, but it appears to predict the osmotic coefficient with a higher accuracy, at least with the present approximations. This is illustrated in Figure 10. Nevertheless the CDH clearly outperforms the cPB in terms of quantitative accuracy for 1:1 salt, although it should be remembered that the CDH data for the mean activity coefficient are *fitted* to the experimental observations.

The corresponding predictions for salt solutions containing multivalent ions, are displayed in Figure 11. An unexpected finding is that the cPB appears to perform better in this case than for monovalent salts. In fact, its accuracy is in this case comparable to that of the CDH.

Note that because the cPB, like PB, is a mean-field theory, it will give erroneous predictions of *structural* behavior in a bulk salt solution. The reason is the inherent approximation at the mean-field level, where it is assumed that the pair correlation functions (between small ions) are unity everywhere. The cPB tries to correct for this in an *effective* manner, by modifying the mean-field potential at short range. Hence, the cPB will, at least in its present simple formulation, fail to predict correct interionic correlation functions. This deficiency is of course

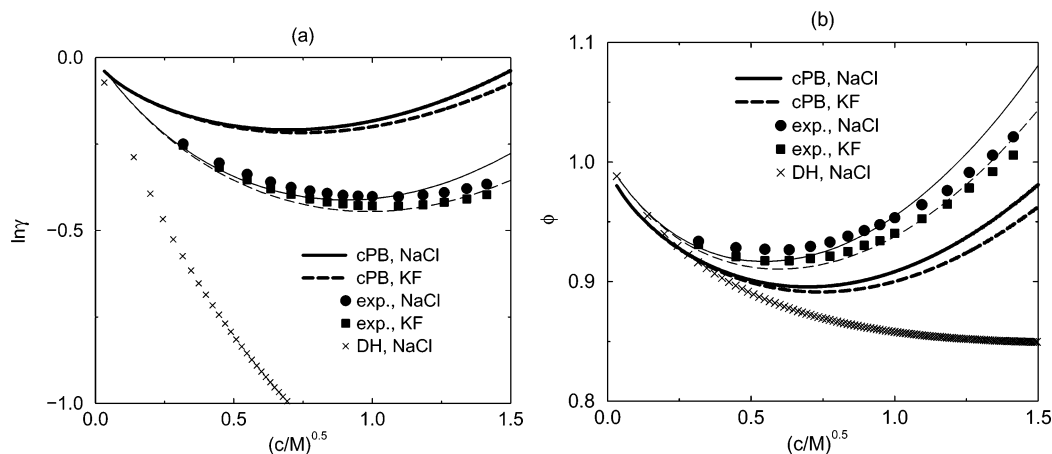


Figure 10. Variation of $\ln \gamma$ and ϕ with the bulk salt concentration, c (in molar units), for various 1:1 salt solutions. Experimental data are given by filled symbols. The notation for CDH predictions is analogous to that for cPB (thick lines) but is instead displayed by thin lines. DH data are only exemplified for NaCl (crosses). CDH data are based on fitted average ionic diameters: $d^{\text{CDH}}(\text{NaCl}) = 3.40 \text{ \AA}$, $d^{\text{CDH}}(\text{KF}) = 3.25 \text{ \AA}$. The cPB and DH data are based on diameters from crystallographic data (Pauling diameters): $d^{\text{P}}(\text{NaCl}) = 2.82 \text{ \AA}$, $d^{\text{P}}(\text{KF}) = 2.71 \text{ \AA}$. These data, the CDH results, and the compiled experimental data are all cited from ref 28.

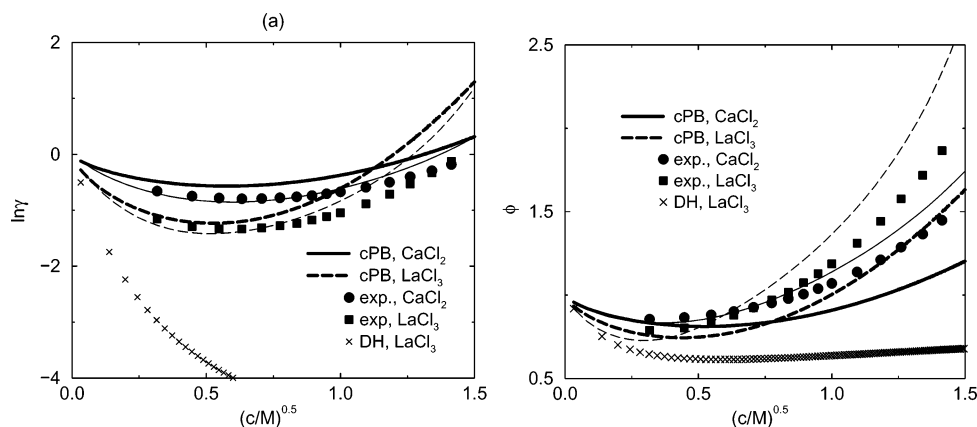


Figure 11. Variation of $\ln \gamma$ and ϕ with the bulk salt concentration, for salt solutions containing multivalent ions. Experimental data are given by filled symbols. The notation for CDH predictions is analogous to that for cPB (thick lines), except that thin lines are used. DH data are only given for LaCl_3 (crosses). CDH data are based on fitted average ionic diameters: $d^{\text{CDH}}(\text{CaCl}_2) = 4.40 \text{ \AA}$, $d^{\text{CDH}}(\text{LaCl}_3) = 4.68 \text{ \AA}$. The cPB and DH data are based on diameters from crystallographic data (Pauling diameters): $d^{\text{P}}(\text{CaCl}_2) = 3.08 \text{ \AA}$, $d^{\text{P}}(\text{LaCl}_3) = 3.31 \text{ \AA}$. These data, the CDH results, and the compiled experimental data are all cited from ref 28.

shared by the ordinary PB theory, although refined formulations have been developed that are able to make more accurate and furthermore symmetric (with respect to interchange of index) predictions, using a symmetric charging process, combined with some approximation of the ionic pair correlation functions.^{58–62} Nevertheless, the very idea behind the cPB is to reduce the shortcomings of the PB in terms of its thermodynamic predictions, with the hope that the effective potential approach can remedy the errors inherent in the mean-field assumption (i.e., neglect of structure), to produce *thermodynamically* accurate results. Note that Figures 3 and 8 do suggest that the cPB nevertheless is able to accurately predict distributions of small ions in strongly asymmetric systems, such as outside, or between, highly charged aggregates. The advantage in those cases is that such highly charged aggregates can be approximated as static suppliers of an external field with which the small ions are allowed to correlate.

In summary, the qualitative agreement with experimental data that is obtained with the cPB, amounts to a substantial improvement in terms of the overall shape of the curves and the physical mechanisms included. Note that the ordinary PB theory gives the following nonphysical predictions: $\ln \gamma = 0$ and $\phi = 1$, irrespective of ion valencies and concentration. The original Debye–Hückel (DH) theory, which contains some

degree of ionic response, does a somewhat better job but is clearly inferior to the cPB, not to mention the CDH. It should also be emphasized that the DH theory is strictly speaking only applicable to solutions with low salt concentrations.⁶³ This is confirmed by the way in which it severely underestimates the activity coefficient, as shown in Figures 10 and 11.

4. Conclusions

By adjusting the interactions between ions at short range, to correct for correlation effects, we have constructed a mean-field theory based on the Poisson–Boltzmann formalism. This “correlation-corrected” Poisson–Boltzmann theory, cPB, produces quantitatively successful predictions for electric double layer systems and qualitatively correct predictions for properties of bulk salt solutions, even at strong electrostatic coupling. Briefly stated, the mentioned potential corrections are (i) a reduction of the mean-field repulsion between ions of like charge and (ii) the introduction of a “hole”, caused by hard core exclusion, in the attractive interaction between ions with charges of opposite sign. The first correction is the most important one, because it enables predictions of correlation attractions between like charged surfaces, in highly coupled systems. The failure of the PB theory to make such qualitative predictions is generally regarded as its most severe flaw. Correction ii is more trivial in

the present formulation, because it simply amounts to the incorporation of the loss of attractive interactions that results from hard core (Pauli) repulsions at close range. We will suggest a possible improvement of this part below.

We have already discussed the fact that there is some ambiguity of the quantitative definition of correction i. However, there are strong physical arguments for its *approximate* appearance. Ion-ion anticorrelations are expected to be important within a range that is roughly equal to the average nearest-neighbor separation. In an electric double layer, this is of course a quantity that varies strongly with the separation to the nearest charged surface. We conjecture that the region very close to the surfaces is the most important one in terms of anticorrelation effects. Hence, we let an estimate of the *minimum* average nearest neighbor separation determine the range of the “correlation potential” in such systems. The encouraging quantitative agreement with simulation data in salt-free systems suggest that this is a reasonable conjecture and that our proposed correction of the mean-field repulsion works quite well, even in strongly coupled systems. We therefore believe that the major source of error in the cPB results we have presented for salt-rich systems, is related to the simplistic way in which correction ii is handled. Note that this correction would be consistent with a steplike radial distribution function, between ions with charges of different sign. In reality, we expect some positive correlation between such ions. This could be included in the cPB formalism by adjusting the effective potential ϕ^{eff} so that it becomes *more attractive* than the pure Coulomb repulsion in a finite region outside $r = d_+ -$. The underestimation of the attractive potential in the present cPB theory is probably the major reason for the exaggerated force oscillations that was predicted for electric double layer system at high concentrations of 2:1 salt (Figure 7). An improvement of the “effective attractive potential” in the cPB theory would most likely reduce this deficiency, but we expect it to have greater impact on predictions of bulk salt properties. To keep things very simple in this initial study, we have chosen not to evaluate various other possibilities for the effective attraction. It would be interesting to do so in future work.

In summary, there is certainly room for improvements of the cPB. Nevertheless, even in its present simple form, it remedies all major flaws of the PB theory, with virtually no increase in theoretical complexity. The latter point is very important, given the wide-spread use of Poisson–Boltzmann calculations, also by researchers whose main expertise lies outside the area of statistical mechanics. Given the crudeness of the primitive model itself, where the molecular nature of the solvent is completely neglected, there appears to be no compelling reason to use complicated, though possibly accurate, theories to describe phenomena at this level of approximation. An appealing feature of the PB theory is that it predicts correct limiting behaviors, such as the force decay between charged surfaces at large separations.⁴ This advantage is retained in the cPB, because such limiting behaviors are unaffected by details of the short-ranged part of the interaction potential. Finally, the thermodynamic consistency of the PB theory, which ensures the validity of sum rules such as the contact value theorem, is also an advantage shared by the cPB.

Acknowledgment. I thank Zareen Abbas for supplying CDH data as well as compiled experimental data on bulk salt solution properties. Torbjörn Åkesson, Bo Jönsson, and Clifford Woodward are also acknowledged for providing valuable comments and criticism.

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