

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/233924585>

Exclusion volume term in the inhomogeneous Poisson–Boltzmann theory for high surface charge

ARTICLE *in* LANGMUIR · JANUARY 2002

Impact Factor: 4.46 · DOI: 10.1021/la011852v

CITATIONS

37

READS

8

2 AUTHORS, INCLUDING:



Christopher W Outhwaite

The University of Sheffield

118 PUBLICATIONS **1,945** CITATIONS

SEE PROFILE

Exclusion Volume Term in the Inhomogeneous Poisson–Boltzmann Theory for High Surface Charge

S. Lamperski[†] and C. W. Outhwaite^{*,‡}

Department of Physical Chemistry, Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland, and Department of Applied Mathematics, University of Sheffield, Sheffield S3 7RH, United Kingdom

Received December 26, 2001. In Final Form: March 13, 2002

A restricted primitive model electrolyte in the neighborhood of a uniformly charged plane electrode is investigated at high surface charge using an improved Poisson–Boltzmann theory. A layering of counterions is found in agreement with Monte Carlo simulations.

Introduction

There has been a renewal of interest in analyzing the inhomogeneous Poisson–Boltzmann (PB) equation in the electric double layer.^{1–5} Attention has focused on correcting the Gouy–Chapman (GC) theory by including ion and solvent size, so that ionic adsorption is not overestimated at high surface charge. Among the areas where there has been interest is that of colloidal dispersions, where the correct description of the electric double layers plays a critical role.^{4,5} In the formalism of classical statistical mechanics, a key term controlling ionic adsorption is the so-called exclusion volume term. This exclusion volume term is the singlet distribution function for an uncharged ion in the presence of the remaining charged ions and electrode. When all the ions and electrode are discharged, the exclusion volume term reduces to the inhomogeneous distribution function for the uncharged system. Recent work has failed to treat adequately this limiting uncharged situation,^{1–5} and the authors⁶ have corrected this failure by using a simple theory for the exclusion volume term. We show here the importance of the exclusion volume term by showing that it plays a critical role in predicting the layering of counterions for a 1:1 electrolyte at high surface charge seen in Monte Carlo (MC) calculations^{7,8} and other theoretical work.^{9–14}

Theory and Discussion

We consider here a restricted primitive model electrolyte with ions of diameter $d = 4$ Å, in the neighborhood of a uniformly charged plane hard wall. When the fluctuation

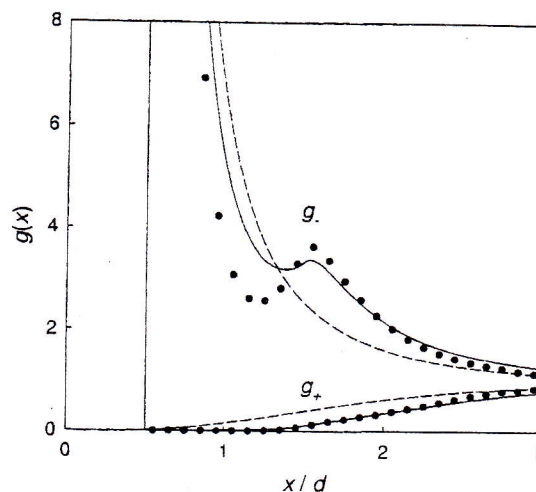


Figure 1. Co-ion and counterion singlet distribution functions for a 1:1 electrolyte at $c = 1$ M, $\sigma = 0.7$ C/m², $d = 4$ Å, $\epsilon = 78.5$, and $T = 298.15$ K. Solid line, present theory; dashed line, GC; solid circles, MC (for 156 counterions and 56 co-ions).

term is neglected,¹⁵ the singlet distribution function $g_i(x)$ for an ion i a normal distance x from the wall into the solution is

$$g_i(x) = \zeta_i \exp(-\beta e_i \psi) \quad (1)$$

where $\zeta_i = g_i(e_i = 0)$ is the exclusion volume term, e_i is the charge of ion i , and ψ is the mean electrostatic potential at x . By considering the analysis of Carnie et al.,¹⁶ the exclusion volume term can be approximated by

$$\ln(\zeta_i/\zeta_i^0) = \int \sum_s n_s c_{is}^0 [g_s - g_s(\sigma = 0)] d\mathbf{r} \quad (2)$$

where σ is the surface charge, $\zeta_i^0 = \zeta_i(\sigma = 0)$, n_s is the mean number density of ions of type s , and c_{is}^0 is the bulk uncharged hard-sphere direct correlation function. Using eq 2 for ζ in eq 1 implies that g_i reduces to ζ_i^0 when the system is fully discharged.

The mean electrostatic potential satisfies Poisson's equation

$$\frac{d^2\psi}{dx^2} = -\frac{1}{\epsilon_0\epsilon} \sum_s e_s n_s g_s(x) \quad (3)$$

where ϵ is the bulk electric permittivity. With g_i given by

- * To whom correspondence should be addressed.
[†] A. Mickiewicz University.
[‡] University of Sheffield.
 (1) Kralj-Iglic, V.; Iglic, A. *J. Phys. II France* **1996**, *6*, 477.
 (2) Borukhov, I.; Andelman, D.; Orland, H. *Phys. Rev. Lett.* **1997**, *79*, 435.
 (3) Borukhov, I.; Andelman, D.; Orland, H. *Electrochim. Acta* **2000**, *46*, 221.
 (4) Trizac, E.; Raimbault, J.-L. *Phys. Rev. E* **1999**, *60*, 6530.
 (5) Hansen, J. P.; Goulding, D.; van Roij, R. *J. Phys. IV France* **2000**, *10*, 27.
 (6) Outhwaite, C. W.; Lamperski, S. *Condens. Matter Phys.* **2001**, *4*, 739.
 (7) Torrie, G. M.; Valleau, J. P. *J. Chem. Phys.* **1980**, *73*, 5807.
 (8) Zhang, L.; White, H. S.; Davis, H. T. *Mol. Simul.* **1992**, *9*, 247.
 (9) Nielaba, P.; Forstmann, F. *Chem. Phys. Lett.* **1985**, *117*, 46.
 (10) Caccamo, C.; Pizzimenti, G.; Blum, L. *J. Chem. Phys.* **1986**, *84*, 3327.
 (11) Kjellander, R.; Marcelja, S. *Chem. Phys. Lett.* **1986**, *127*, 402.
 (12) Plishke, M.; Henderson, D. *J. Chem. Phys.* **1988**, *88*, 2712.
 (13) Mier-y-Teran, L.; Suh, S. H.; White, H. S.; Davis, H. T. *J. Chem. Phys.* **1990**, *92*, 5087.
 (14) Patra, C. N. *J. Chem. Phys.* **1999**, *111*, 9832.

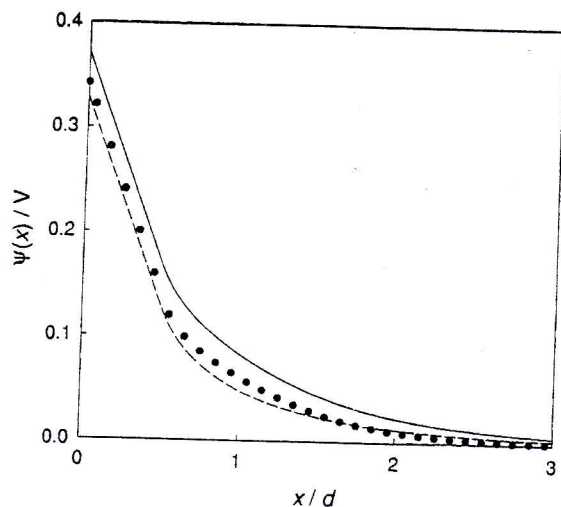


Figure 2. Mean electrostatic potential corresponding to the parameters of Figure 1.

eq 1, we have a closed system of equations for ψ on specifying ζ_i^0 and c_{is}^0 . For ease, we take the discharged functions to be given by the hard-sphere analytic Percus–Yevick values.^{17,18}

The equations were solved using a previously derived quasi-linearization technique.¹⁹ In Figure 1, we give the singlet distribution functions for a 1 M 1:1 electrolyte at $\sigma = 0.7$ C/m² and $\epsilon = 78.5$ with the corresponding MC values and the GC theory incorporating the distance of closest approach. At this surface charge, the MC results predict a shoulder in the counterion distribution function

at $x \sim 1.5d$, indicating a second layer. Although not so pronounced, the present theory also predicts a layering of the counterions at the same value of x . As the GC theory neglects ion size, except for the distance of closest approach, it is unable to capture this layering. The inclusion of the exclusion volume term also means that the co-ion distribution function is accurately represented. Figure 2 displays the corresponding mean electrostatic potential at $\sigma = 0.7$ C/m². The integrated distribution functions lead to a smooth monotonic decreasing potential which hides the underlying structure of the double layer. Indeed, the errors in the GC distribution functions are essentially canceled out leading to a better description of the MC values.

Conclusion

The overall interplay between steric and charge effects is very complex. At intermediate values of the surface charge and electrolyte concentration for monovalent ions, an accurate description depends on an adequate treatment of both the fluctuation and exclusion volume terms.¹⁵ At the high surface charge considered here, the steric effect becomes very important. An earlier treatment¹⁹ described the exclusion volume term by the uncharged hard-sphere distribution function. This description is unsatisfactory as at high surface charge the surface charge is driving the double-layer structure. For the parameters treated here, the fluctuation term is apparently of lower order, although clearly it is of importance for accurately predicting the finer details of the counterion distribution. Indeed, as the ion size increases for the 1:1 electrolyte at fixed surface charge and electrolyte concentration, the present theory becomes increasingly inaccurate, and the fluctuation term must also be treated.

Acknowledgment. Financial support from Adam Mickiewicz University, Faculty of Chemistry, is appreciated.

LA011852V

(15) Carnie, S. L.; Torrie, G. M. *Adv. Chem. Phys.* **1984**, *56*, 141.

(16) Carnie, S. L.; Chan, D. Y. C.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Phys.* **1981**, *74*, 1472.

(17) Henderson, D.; Abraham, F. F.; Barker, J. A. *Mol. Phys.* **1976**, *31*, 1291.

(18) Hansen, J. P.; McDonald, I. R. *The Theory of Simple Liquids*, 2nd ed.; Academic Press: London, 1990.

(19) Lamperski, S.; Outhwaite, C. W. *J. Electroanal. Chem.* **1999**, *460*, 135.