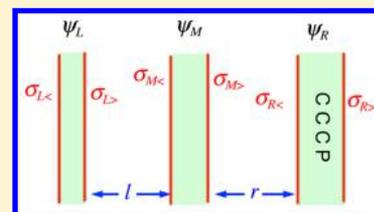


Electric Double-Layer Interaction between Dissimilar Charge-Conserved Conducting Plates

Derek Y. C. Chan^{*,†,‡}[†]Particulate Fluids Processing Centre, School of Mathematics and Statistics, The University of Melbourne, Parkville, Victoria 3010, Australia[‡]Department of Chemistry and Biotechnology, Swinburne University of Technology, Hawthorn, Victoria 3122, Australia

Supporting Information

ABSTRACT: Small metallic particles used in forming nanostructured to impart novel optical, catalytic, or tribo-rheological can be modeled as conducting particles with equipotential surfaces that carry a net surface charge. The value of the surface potential will vary with the separation between interacting particles, and in the absence of charge-transfer or electrochemical reactions across the particle surface, the total charge of each particle must also remain constant. These two physical conditions require the electrostatic boundary condition for metallic nanoparticles to satisfy an equipotential whole-of-particle charge conservation constraint that has not been studied previously. This constraint gives rise to a global charge conserved constant potential boundary condition that results in multibody effects in the electric double-layer interaction that are either absent or are very small in the familiar constant potential or constant charge or surface electrochemical equilibrium condition.



INTRODUCTION

In the venerable Derjaguin–Landau¹–Verwey–Overbeek² theory of the interaction between nanoparticles in solution, the electrostatic interaction between charged particles is calculated according to a mean-field model in which the spatial disposition of mobile solution ions is governed by the Boltzmann distribution according to the mean electrostatic potential. The mean potential is, in turn, determined by solving the Poisson equation, thus giving rise to the Poisson–Boltzmann model for the electric double-layer interaction. This description requires specification of the electrostatic boundary condition at the particle–solution interface. Traditionally, the surface potential or the surface charge density is assumed to be known and independent of particle separation, corresponding to the so-called constant potential or constant charge boundary condition. Despite such rather simplistic assumptions, the details of the electrical interaction can still be quite rich and complex.^{3,4} Information about the mechanism of the development surface charge, for example, due to the ionization of acidic/basic⁵ or amphoteric⁶ surface groups, can also be incorporated in a self-consistent manner into the electrostatic boundary condition so that both the surface charge and the surface potential will change with the separation between the interacting particles. This is often referred to as charge regulation; however, all of such boundary conditions—be they constant potential, constant charge, or charge regulation—follow from specifying *local* electrochemical behavior of the interface.

For conducting nanoparticles where there is an absence of surface charge-transfer mechanisms, a new *global* boundary condition would apply. As the separation between interacting particles changes, the surface of individual conducting particles will remain an equipotential surface; however, the value of the

potential will change with separation as a result of electric double-layer interactions. The absence of surface charge-transfer mechanisms means that the total charge carried by the particle must remain constant, whereas the surface charge density on the interacting particles will vary along the surface to maintain a constant surface potential. Thus, the appropriate electrostatic boundary condition will be a constraint between the value of the potential on the equipotential surface and the total charge on each particle at all separations between the particles. We term this a charge conserved constant potential (CCCCP) boundary condition that can give rise to novel multibody and possibly long-ranged electrostatic effects. Recently, similar models have been proposed to model electrodes in simulation studies.^{7,8}

THEORY

To maintain the physical perspicacity of the discussion and to illustrate how the CCCC boundary condition is used and its physical consequences, we consider the electrical double-layer interaction under the CCCC boundary condition in a 1:1 electrolyte in the linearized Poisson–Boltzmann or Debye–Hückel limit. This allows a clear illustration of how the CCCC boundary condition is to be applied and at the same time yield simple analytic results that are informative without any loss of new physical insight. This simple model also illustrates how the CCCC boundary condition can give rise to novel multibody and long-ranged electrostatic effects. The steps needed to extend to the nonlinear Poisson–Boltzmann model will be clear even

Received: July 28, 2015

Revised: August 26, 2015

though the necessary numerical steps required may be more cumbersome.

Consider two dissimilar charge-conserved conducting particles that are parallel plates labeled “L” (left) and “R” (right), with thickness t_L and t_R at a separation, l , as illustrated in Figure 1.

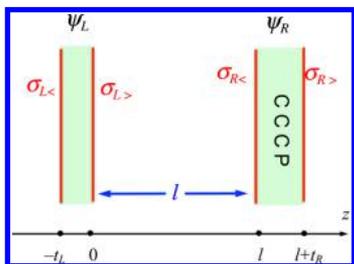


Figure 1. Schematic diagram of two plates L and R at separation l , with the charged conserved constant potential (CCCCP) boundary condition. The plates have constant surface potentials ψ_L and ψ_R and surface charge densities $\sigma_{L<}$, $\sigma_{L>}$, $\sigma_{R<}$ and $\sigma_{R>}$ at the indicated faces. The plates have thickness t_L and t_R .

They are immersed in equilibrium with a 1:1 electrolyte of bulk molar concentration c_B (M/L) or bulk ion number density, n_B (m^{-3}) = $10^3 N_A c_B$, where N_A is Avogadro's number. The 1D Debye–Hückel equation for the electrostatic potential, $\phi(z)$ at position z is $d^2\phi/dz^2 - \kappa^2\phi = 0$, where $\kappa = (2n_B q^2 / \epsilon \epsilon_0 k_B T)^{1/2}$ is the usual inverse Debye length where q is the elementary charge, ϵ and ϵ_0 are the permittivity of the solution and of free space, k_B is the Boltzmann constant, and T is the absolute temperature. The solution of the Debye–Hückel equation for the potential in the electrolyte is

$$\phi(z) = \psi_L(l) \exp(\kappa[z + t_L]), \quad -\infty < z \leq -t_L \quad (1a)$$

$$\phi(z) = \psi_L(l) \frac{\sinh(\kappa[l - z])}{\sinh(\kappa l)} + \psi_R(l) \frac{\sinh(\kappa z)}{\sinh(\kappa l)}, \quad 0 \leq z \leq l \quad (1b)$$

$$\phi(z) = \psi_R(l) \exp(-\kappa(z - [l + t_R])), \quad l + t_R \leq z < \infty \quad (1c)$$

In the interior of each of the conducting plates the potential is a constant. The solution in eq 1 reflects the fact that the interior surfaces (facing the opposing plate) and the exterior surface (facing the bulk electrolyte) of the CCCC plate L or R have the same potential, $\psi_L(l)$ or $\psi_R(l)$, whose value varies with separation, l . However, the surface charge densities at the four surfaces ($\sigma_{L<}$, $\sigma_{L>}$, $\sigma_{R<}$ and $\sigma_{R>}$; see Figure 1 for definition) will all be different and will vary with the plate separation. The surface charge densities on plate L are

$$\begin{aligned} \sigma_{L>}(l) &= -\epsilon \epsilon_0 \left[\frac{d\phi}{dz} \right]_{z=0} \\ &= -\epsilon \epsilon_0 \kappa \left[-\psi_L(l) \frac{\cosh(\kappa l)}{\sinh(\kappa l)} + \psi_R(l) \frac{1}{\sinh(\kappa l)} \right] \end{aligned} \quad (2a)$$

$$\sigma_{L<}(l) = \epsilon \epsilon_0 \left[\frac{d\phi}{dz} \right]_{z=-t_L} = \epsilon \epsilon_0 \kappa \psi_L(l) \quad (2b)$$

and on plate R are

$$\begin{aligned} \sigma_{R<}(l) &= \epsilon \epsilon_0 \left[\frac{d\phi}{dz} \right]_{z=l} \\ &= \epsilon \epsilon_0 \kappa \left[-\psi_L(l) \frac{1}{\sinh(\kappa l)} + \psi_R(l) \frac{\cosh(\kappa l)}{\sinh(\kappa l)} \right] \end{aligned} \quad (3a)$$

$$\sigma_{R>}(l) = -\epsilon \epsilon_0 \left[\frac{d\phi}{dz} \right]_{z=l+t_R} = \epsilon \epsilon_0 \kappa \psi_R(l) \quad (3b)$$

The electrical properties of the plates are determined by specifying either the surface charge density ($\sigma_L(\infty)$, $\sigma_R(\infty)$) or the surface potential ($\psi_L(\infty)$, $\psi_R(\infty)$) of each plate when they are far apart ($l \rightarrow \infty$), where the charge and potential in this limit are related by $\sigma(\infty) = (\kappa/\epsilon \epsilon_0) \psi(\infty)$. The condition of charge conservation is $\sigma_{<}(l) + \sigma_{>}(l) = 2 \sigma(\infty)$ and has to be applied for each plate to determine the variation of its surface potentials with separation, l . On using eqs 1–3 and after some algebra, we obtain the relation for the variation of the surface potential of each plate with separation, l . (See the Supporting Information for details.)

$$\psi_L(l) = \psi_L(\infty) + \psi_R(\infty) e^{-\kappa l} \quad (4a)$$

$$\psi_R(l) = \psi_R(\infty) + \psi_L(\infty) e^{-\kappa l} \quad (4b)$$

The surface charge densities on the surfaces of plate L and R can be obtained from eq 2 and 3

$$\sigma_{L>}(l) = \epsilon \epsilon_0 \kappa [\psi_L(\infty) - \psi_R(\infty) e^{-\kappa l}] \quad (5a)$$

$$\sigma_{L<}(l) = \epsilon \epsilon_0 \kappa [\psi_L(\infty) + \psi_R(\infty) e^{-\kappa l}] \quad (5b)$$

$$\sigma_{R<}(l) = \epsilon \epsilon_0 \kappa [\psi_R(\infty) - \psi_L(\infty) e^{-\kappa l}] \quad (5c)$$

$$\sigma_{R>}(l) = \epsilon \epsilon_0 \kappa [\psi_R(\infty) + \psi_L(\infty) e^{-\kappa l}] \quad (5d)$$

We see from eq 4 that in the limit of small separations ($l \rightarrow 0$) the surface potential of both plates approaches the common value: $\psi_L(l \rightarrow 0) = \psi_R(l \rightarrow 0) = \psi_L(\infty) + \psi_R(\infty)$, that is the sum of the surface potentials of the two plates at infinite separation. From eq 5, we see that in the limit $l \rightarrow 0$, the surface charge densities of the touching inner surfaces will become equal in magnitude but opposite in sign, that is, $\sigma_{L>}(l \rightarrow 0) + \sigma_{R<}(l \rightarrow 0) = 0$, as expected from electroneutrality considerations. The magnitude of the surface charge is the difference between the surface charges at infinite separation: $\sigma_{L>}(l \rightarrow 0) \rightarrow \sigma_L(\infty) - \sigma_R(\infty)$ and $\sigma_{R<}(l \rightarrow 0) \rightarrow \sigma_R(\infty) - \sigma_L(\infty)$. As a result of charge conservation on each plate, the surface charge densities on the outer surfaces of each plate will approach the same value, namely, the sum of the surface charge density on each at infinite separation: $\sigma_{L<}(l \rightarrow 0) \rightarrow \sigma_L(\infty) + \sigma_R(\infty)$ and $\sigma_{R>}(l \rightarrow 0) \rightarrow \sigma_L(\infty) + \sigma_R(\infty)$. It is also easy to verify from the simple explicit results in eq 5 that the surface charge densities on each plate conditions: $\sigma_{L<}(l) + \sigma_{L>}(l) = 2 \sigma_L(\infty) = 2[\epsilon \epsilon_0 \kappa \psi_L(\infty)]$ and $\sigma_{R<}(l) + \sigma_{R>}(l) = 2 \sigma_R(\infty) = 2[\epsilon \epsilon_0 \kappa \psi_R(\infty)]$. In the special case of identically charged plates in the limit $l \rightarrow 0$, the surface charge densities of the touching inner surfaces will become zero.

The repulsive electrical double-layer disjoining pressure, $\Pi_{\text{CCCCP}}(l)$, between the interacting plates that obeys the CCCC boundary condition can be expressed as the usual sum of the osmotic and electrostatic stress given by³

$$\Pi_{\text{CCCP}}(l) = \frac{\varepsilon\varepsilon_0}{2} \left\{ \kappa^2 \phi^2 - \left(\frac{d\phi}{dz} \right)^2 \right\} \quad (6a)$$

$$= 2\varepsilon\varepsilon_0 \kappa^2 \psi_L(\infty) \psi_R(\infty) e^{-\kappa l} \quad (6b)$$

where the general Debye–Hückel expression in {...} can be evaluated at any z value in the range $0 \leq z \leq l$, and eq 6b follows from using eq 1. It is quite remarkable that the complexity of the charge conserved constant potential boundary yields a surprisingly simple result of a simple exponential for the disjoining pressure. Consider the special limit of identical surfaces where $\psi_L(\infty) = \psi(\infty) = \psi_R(\infty)$, the simple exponential dependence on separation found for $\Pi_{\text{CCCP}}(l)$ in eq 6 can be compared with the disjoining pressure under the more familiar constant surface potential, $\Pi_{\text{pot}}(l)$, or constant surface charge, $\Pi_{\text{chg}}(l)$, boundary conditions that are given by³

$$\Pi_{\text{pot}}(l) = 2\varepsilon\varepsilon_0 \kappa^2 \psi^2(\infty) \frac{e^{-\kappa l}}{(1 \pm e^{-\kappa l})^2} \quad (7)$$

Unlike the constant charge case, the repulsion between CCCP particles is finite for all separations with a magnitude that is intermediate between that of the constant charge and the constant potential case. The interaction free energy per unit area obtained by integrating the disjoining pressure $\Pi_{\text{CCCP}}(l)$ over the separation also has a simple exponential dependence on separation.

To illustrate many body effects of the CCCP boundary condition on electric double-layer interactions, we consider the a three-plate system: “L” (left), “M” (middle), and “R” (right), at separations l and r between them as illustrated in Figure 2. Now

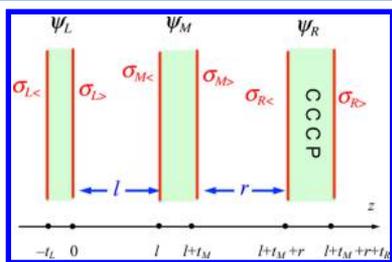


Figure 2. Schematic diagram of three plates L, M, and R at separation l and r with the charged conserved constant potential (CCCP) boundary condition. The plates have constant surface potentials ψ_L , ψ_M , and ψ_R and surface charge densities $\sigma_{L<}$, $\sigma_{L>}$, $\sigma_{M<}$, $\sigma_{M>}$, $\sigma_{R<}$, and $\sigma_{R>}$ at the indicated faces. The plates have thickness t_L , t_M , and t_R .

under the constant potential boundary conditions, the interaction between plates L and M depends only on their separation l but is independent of the distance r , namely, the position of plate R. This is not the case for the CCCP boundary condition in which the electrostatic potential in the four regions of the electrolyte has the form (see Figure 2 for the definition of symbols)

$$\begin{aligned} \phi(z) &= \psi_L(l, r) \exp(\kappa[z + t_L]), & -\infty < z < -t_L \\ \phi(z) &= \psi_L(l, r) \frac{\sinh(\kappa[l - z])}{\sinh(\kappa l)} + \psi_M(l, r) \frac{\sinh(\kappa z)}{\sinh(\kappa l)}, & 0 \leq z \leq l \\ \phi(z) &= \psi_M(l, r) \frac{\sinh(\kappa[r - x])}{\sinh(\kappa r)} + \psi_R(l, r) \frac{\sinh(\kappa x)}{\sinh(\kappa r)}, & 0 \leq x \leq r \\ \phi(z) &= \psi_R(l, r) \exp(-\kappa y), & y \geq 0 \end{aligned} \quad (8)$$

where $x \equiv z - (l + t_M)$ and $y \equiv z - (l + t_M + r + t_R)$ to simplify the notation. In eq 8, we exhibit the dependence of the surface potentials of the three plates: $\psi_L(l, r)$, $\psi_M(l, r)$, and $\psi_R(l, r)$ on the plate spacing l and r . These three surface potentials are determined by imposing the charge conservation condition on each plate. The six different surface charge densities on the three plates are first obtained using Gauss’s Law from the derivative of the potential given in eq 8 evaluated at each surface. The application of the surface charge conservation for each of the three plates then gives a set of coupled equations from which we can determine the dependence of ψ_L , ψ_M , and ψ_R on the separations l and r and in terms of the values of the surface potentials when the plates are infinitely far from each other: $\psi_L(\infty)$, $\psi_M(\infty)$, and $\psi_R(\infty)$. The explicit results are (see Supporting Information for details)

$$\psi_L(l, r) = \psi_L(\infty) + [\psi_M(\infty) + \psi_R(\infty)e^{-\kappa r}]e^{-\kappa l} \quad (9a)$$

$$\psi_M(l, r) = \psi_M(\infty) + \psi_L(\infty)e^{-\kappa l} + \psi_R(\infty)e^{-\kappa r} \quad (9b)$$

$$\psi_R(l, r) = \psi_R(\infty) + [\psi_M(\infty) + \psi_L(\infty)e^{-\kappa l}]e^{-\kappa r} \quad (9c)$$

Using eq 6a, the disjoining pressure Π_{LM} between the L and M plate is

$$\Pi_{\text{LM}}(l, r) = 2\varepsilon\varepsilon_0 \kappa^2 \psi_L(\infty) [\psi_M(\infty) + \psi_R(\infty)e^{-\kappa r}]e^{-\kappa l} \quad (10)$$

and that between the M and R plate is

$$\Pi_{\text{MR}}(l, r) = 2\varepsilon\varepsilon_0 \kappa^2 \psi_R(\infty) [\psi_M(\infty) + \psi_L(\infty)e^{-\kappa l}]e^{-\kappa r} \quad (11)$$

In particular, we can see that the disjoining pressure Π_{LM} between plates L and M depends on the position of plate R, via an “effective potential” $\psi_M^{\text{eff}}(r) \equiv [\psi_M(\infty) + \psi_R(\infty)e^{-\kappa r}]$ of plate M that varies with the position of plate R through the spacing r (see eq 10 and Figure 2). Similarly, the disjoining pressure Π_{MR} between plates M and R depends on the position of plate L (see eq 11 and Figure 2). Thus, even in a simple 1D system, the charge-conserved constant potential condition can give rise to three-body effects. In contrast, three-body effects are not present with the constant potential boundary condition; with the constant charge boundary condition, the high dielectric permittivity of the aqueous phase means that three-body effects are very weak.

CONCLUSIONS

By studying a simple 1D system in detail, we have demonstrated how to calculate the electrical double-layer interactions involving charged conserved constant potential plates. The physically perspicuous analytical results of remarkably symmetry and simplicity illustrate the fundamental differences from the conventional constant potential, constant charge, or charge regulation boundary conditions. The CCCP condition imposes a constraint on the total charge on every particle involved in the interaction rather than being a local condition applied at the particle surface. One consequence we saw, even with the simple one-dimensional model, is the emergence of many-body effects that can be long-ranged in the limit of small particles or low electrolyte concentration. Although the linear Debye–Hückel model used in the present paper is strictly only valid when the potentials are smaller than the thermal value (kT/q) ≈ 25 mV, in practice, the numerical errors of this model are still quite acceptable for potentials up to 50 mV. The analytical nature of

the Debye–Hückel model facilitates the exhibition of key physical effect without excessive mathematical details or numerical complexities.

At a given spatial configuration of nanoparticles, the imposition of this constraint will, in general, involve a summation or integration of the surface charge distribution of each individual particle to determine the surface potential of each particle. As we have seen in the simple three-plate example, this couples the properties on all of the particles and represents a *global* constraint on the differential equation rather than just the more familiar local boundary condition. It is the global nature of such constraints that can give rise to the elucidated many-body effect.

Although the 1D results obtained for interacting plates can under certain conditions be used with the Derjaguin approximation to give the interaction between particles of different geometries, a rigorous application of the CCCP boundary condition to interacting 3-D particulate systems involves calculating the total charge on individual particles and finding the corresponding surface potentials self-consistently. This suggests that the solution of the potential problem by a boundary integral method might be an effective approach.⁹ This is a development that will be explored in a future publication.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.langmuir.5b02796](https://doi.org/10.1021/acs.langmuir.5b02796).

Details of the derivations of results given here. ([PDF](#))

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: D.Chan@unimelb.edu.au.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported in part by an Australian Research Council Discovery Project Grant.

■ REFERENCES

- (1) Derjaguin, B. V.; Landau, L. D. Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solution of electrolytes. *Acta Physicochim. URSS*. **1941**, *14*, 633–662.
- (2) Verwey, E. J. W.; Overbeek, J. Th. G.; Verwey, E. J. W. *Theory of the Stability of Lyophobic Colloids*; Elsevier: Amsterdam, 1948.
- (3) Parsegian, V. A.; Gingell, D. On the electrostatic interaction across a salt solution between two bodies bearing unequal charges. *Biophys. J.* **1972**, *12*, 1192–1204.
- (4) McCormack, D.; Carnie, S. L.; Chan, D. Y. C. Calculation of electric double layer force and interaction energy between dissimilar surfaces. *J. Colloid Interface Sci.* **1995**, *169*, 177–196.
- (5) Ninham, B. W.; Parsegian, V. A. Electrostatic potential between surfaces bearing ionizable groups in ionic equilibrium with physiologic saline solution. *J. Theor. Biol.* **1971**, *31*, 405–428.
- (6) Chan, D. Y. C.; Healy, T. W.; White, L. R. Electrical double layer interactions under regulation by surface ionisation equilibria – dissimilar amphoteric surfaces. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2844–2865.
- (7) Reed, S. K.; Lanning, O. J.; Madden, P. A. Electrochemical interface between an ionic liquid and a model metallic electrode. *J. Chem. Phys.* **2007**, *126*, 084704.
- (8) Wang, Z.; Yang, Y.; Olmsted, D. L.; Asta, M.; Laird, B. B. Evaluation of the constant potential method in simulating electric double-layer capacitors. *J. Chem. Phys.* **2014**, *141*, 184102.
- (9) McCartney, L. N.; Levine, S. An improvement on the Derjaguin's expression at small potentials for the double layer interaction energy of two spherical colloidal particles. *J. Colloid Interface Sci.* **1969**, *30*, 345–354.