

Exact Analytic Result of Contact Value for the Density in a Modified Poisson–Boltzmann Theory of an Electrical Double Layer

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Abstract: For a simple modified Poisson–Boltzmann (SMPB) theory, taking into account the *finite ionic size*, we have derived the exact analytic expression for the contact values of the difference profile of the counterion and co-ion, as well as of the sum (density) and product profiles, near a charged planar electrode that is immersed in a binary symmetric electrolyte. In the *zero ionic size* or *dilute* limit, these contact values reduce to the contact values of the Poisson–Boltzmann (PB) theory. The analytic results of the SMPB theory, for the difference, sum, and product profiles were compared with the results of the Monte-Carlo (MC) simulations [Bhuiyan, L. B.; Outhwaite, C. W.; Henderson, D. J. *Electroanal. Chem.* **2007**, *607*, 54; Bhuiyan, L. B.; Henderson, D. J. *Chem. Phys.* **2008**, *128*, 117101], as well as of the PB theory. In general, the analytic expression of the SMPB theory gives better agreement with the MC data than the PB theory does. For the difference profile, as the electrode charge increases, the result of the PB theory departs from the MC data, but the SMPB theory still reproduces the MC data quite well, which indicates the importance of including steric effects in modeling diffuse layer properties. As for the product profile, (i) it drops to *zero* as the electrode charge approaches *infinity*; (ii) the speed of the drop increases with the *ionic size*, and these behaviors are in contrast with the predictions of the PB theory, where the product is identically 1.

Introduction

Exact relations are always interesting per se from a theoretical perspective. Besides, they aid theoretical development by serving as checks and can be useful tools in assessing different theories. In the theory of an electrical double layer, such relations are the so-called *contact theorems*.^{1–4} For example, for a binary symmetric electrolyte with ion diameter a , assuming that the planar electrode has a negative charge, the contact values of the density,^{1,2} charge,^{3–5} and product^{3,4} profiles are given by^{1,3,4,6}

$$g_{\text{sum}}(a/2) = \alpha + \frac{b^2}{2} \quad (1)$$

$$g_{\text{diff}}(a/2) = \mathcal{J} + \frac{b^2}{2} \quad (2)$$

and

$$g_{-}(a/2)g_{+}(a/2) = \alpha^2 - \mathcal{J}^2 + b^2(\alpha - \mathcal{J}) \quad (3)$$

respectively, where $g_{\text{sum}}(x) = 1/2[g_{+}(x) + g_{-}(x)]$ and $g_{\text{diff}}(x) = 1/2[g_{+}(x) - g_{-}(x)]$, with the subscripts sum and diff denoting sum and difference. $g_{-}(x)$ and $g_{+}(x)$ are the singlet distribution functions for the co-ions (ions with same sign as the surface charge of the electrode) and the counterions (ions with opposite sign to the surface charge of the electrode), respectively. $\mathcal{J} = -\beta ze \int_{a/2}^{\infty} dx [\partial\psi(x)/\partial x]g_{-}(x)$, where $\psi(x)$ is the electrostatic potential. $b = 2\pi\beta\sigma^2/c_b\epsilon$ is

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the dimensionless electrode charge density, whose dimensioned value is σ .⁷ $\alpha = \beta P/2c_b$ and is the osmotic coefficient of the bulk electrolyte, and P the bulk electrolyte pressure. $\beta = 1/k_B T$ (k_B is the Boltzmann constant and T the absolute temperature). e , z , c_b , and ϵ are the elementary charge, the absolute value of the valence of an ion, the bulk concentration of the ions, and the dielectric constant, respectively. It should be mentioned that the contact value of eq 1 is also valid for an asymmetric electrolyte, which was first derived by Henderson et al.¹

Recently Bhuiyan et al. examined the contact values of the profiles of the double layer formed by the electrolyte species in a binary symmetric restricted primitive model (RPM) electrolyte next to a planar electrode by means of the Monte Carlo (MC) simulation. They focused on the product profile, instead of the density profile or the charge profile. Because, at large electrode charge, the contact values of these profiles are dominated by the large quadratic term in the electrode charge, it is difficult to extract detailed information from the simulations. Note that in the Poisson–Boltzmann (PB) theory, the counterion and co-ion profiles are exponentials of $\exp[\pm ze\psi(x)/k_B T]$,⁸ so its product is identically 1.⁷ However, they found that the MC simulation value is not 1 nor even a constant as the electrode charge is varied. The product profile of PB prediction does not agree qualitatively with the simulation result.⁷ This is a direct test of the basis of the PB theory.

On the other hand, the finite ionic size may play an important role in a concentrated solution. Since Bikerman⁹ first showed that the deviation of the distribution function from Boltzmann's function takes into account the proper volume of the ions, there followed a lot of works.^{9–23} For a very comprehensive review of previous works, excellent recent papers^{21,22} should be referred to. The simple modified Poisson–Boltzmann (SMPB) model of Kornyshev²³ and Kilic et al.^{21,22} for steric effects in electrolytes has been reinvented many times by Borukhov et al.,^{15,16} Iglic,¹⁴ and Eigen and Wicke,¹² and also by Dutta.¹⁰ Thus, the following question arises: Can the SMPB theory reproduce Bhuiyan, Outhwaite, and Henderson's MC data?⁷ This will give a direct test of the basis of the SMPB theory.

Model and Theory

On the basis of mean-field theory together with the lattice-gas approximation in statistical mechanics,^{15,16} the phenomenological free energy of a general electrolyte system can be written as^{15,16,24}

$$\Omega = \frac{\epsilon}{8\pi} \int d^3\mathbf{r} (\nabla\psi(\mathbf{r}))^2 - \int d^3\mathbf{r} \sum_i^m \mu_i c_i(\mathbf{r}) + \frac{k_B T}{a^3} \int d^3\mathbf{r} \left[\left(1 - \sum_i^m c_i(\mathbf{r}) a^3 \right) \times \ln \left(1 - \sum_i^m c_i(\mathbf{r}) a^3 \right) + \sum_i^m c_i(\mathbf{r}) a^3 \ln(c_i(\mathbf{r}) a^3) \right] + \int d^3\mathbf{r} \lambda(\mathbf{r}) + \frac{4\pi}{\epsilon} \sum_i^m e z_i c_i(\mathbf{r}) \quad (4)$$

where $c_i(\mathbf{r})$, μ_i , and z_i are the local concentration, the chemical potential, and the valence of the ionic species i ($i = 1, \dots, m$), respectively. a is the effective size of the ions and solvent molecules. The term $(k_B T)/a^3 \int d^3\mathbf{r} (1 - \sum_i^m c_i(\mathbf{r}) a^3) \ln(1 - \sum_i^m c_i(\mathbf{r}) a^3)$ is the entropy of the solvent molecules that is responsible for the steric corrections to the PB equation.^{15,16}

The last two terms in eq 4, containing the Lagrange multiplier $\lambda(\mathbf{r})$, allow us to regard the local concentration, $c_i(\mathbf{r})$, and the electrostatic potential, $\psi(\mathbf{r})$, as independent fields. Following the method in ref 24 we can obtain

$$\nabla^2 \psi(\mathbf{r}) = -\frac{4\pi e}{\epsilon} \sum_i^m z_i c_i(\mathbf{r}) \quad (5)$$

with

$$c_i(\mathbf{r}) = \frac{c_{ib} \exp(-\beta e z_i \psi(\mathbf{r}))}{1 - \sum_i^m c_{ib} a^3 + \sum_i^m c_{ib} a^3 \exp(-\beta e z_i \psi(\mathbf{r}))} \quad (6)$$

where $i = 1, \dots, m$ and c_{ib} is the bulk concentration of the ionic species i . Equations 5 and 6 are the SMPB equations. Notice that in the *zero size* ($a \rightarrow 0$) or *dilute limit* ($c_{ib} \rightarrow 0$), eqs 5 and 6 are reduced to the PB equation.⁸ It should be pointed out that just like the PB equation, eqs 5 and 6 can be applied to any geometry and boundary conditions.

Here, for comparison with the results of the MC simulations of Bhuiyan et al.,⁷ we also consider a binary symmetric electrolyte and assume, without loss of generality, that the planar electrode has a negative charge. Thus, we have $m = 2$, $z_1 = z$, $z_2 = -z$, $c_{1b} = c_{2b} = c_b$, and eqs 5 and 6 are reduced to

$$\frac{d^2 \psi(x)}{dx^2} = \frac{8z\pi e c_b}{\epsilon} \frac{\sinh(ze\beta\psi(x))}{1 + 2\rho^* \sinh^2\left(\frac{ze\beta\psi(x)}{2}\right)} \quad (7)$$

where $\rho^* = 2c_b a^3$ is the reduced density, and x is the perpendicular distance of the ion from the electrode surface. The singlet distribution functions for the counterions and the co-ions, which are calculated by $g_+(x) = c_1(x)/c_b$ and $g_-(x) = c_2(x)/c_b$, are given by

$$g_+(x) = \frac{\exp(ze\beta\psi(x))}{1 + 2\rho^* \sinh^2\left(\frac{ze\beta\psi(x)}{2}\right)} \quad (8)$$

and

$$g_-(x) = \frac{\exp(-ze\beta\psi(x))}{1 + 2\rho^* \sinh^2\left(\frac{ze\beta\psi(x)}{2}\right)} \quad (9)$$

respectively.

Then, the difference profile $\{1/2[g_+(x) - g_-(x)]\}$ is given by

$$g_{\text{diff}}(x) = \frac{\sinh(ze\beta\psi(x))}{1 + 2\rho^* \sinh^2\left(\frac{ze\beta\psi(x)}{2}\right)} \quad (10)$$

The sum profile $\{1/2[g_+(x) + g_-(x)]\}$ is given by

$$g_{\text{sum}}(x) = \frac{\cosh(ze\beta\psi(x))}{1 + 2\rho^* \sinh^2\left(\frac{ze\beta\psi(x)}{2}\right)} \quad (11)$$

It should be pointed out that the sign of the charge of the electrode is immaterial to the definition of $g_{\text{diff}}(x)$. However, for the sake of definiteness, we have assumed that the electrode has a negative charge and $g_{\text{diff}}(x)$ is either positive or mostly positive (with a positive area). Thus, the individual ion profiles are the sum (for the counterions) and difference (for the co-ions) of $g_{\text{sum}}(x)$ and $g_{\text{diff}}(x)$, i.e., $g_+(x) = g_{\text{sum}}(x) + g_{\text{diff}}(x)$ and $g_-(x) = g_{\text{sum}}(x) - g_{\text{diff}}(x)$.

The product profile is given by

$$g_-(x)g_+(x) = \frac{1}{\left[1 + 2\rho^* \sinh^2\left(\frac{ze\beta\psi(x)}{2}\right)\right]^2} \quad (12)$$

Following the trick in refs 21–23, i.e., integrating eq 7 using the boundary conditions $\psi(x)|_{x=a/2} = \psi_D$, $\psi(x)|_{x \rightarrow \infty} = 0$, and $d\psi(x)/dx|_{x \rightarrow \infty} = 0$, we can get

$$\sigma = -\sqrt{\frac{c_b \epsilon}{\pi \beta \rho^*}} \sqrt{\ln \left[1 + 2\rho^* \sinh^2\left(\frac{ze\beta\psi_D}{2}\right) \right]} \quad (13)$$

where $\sigma = -\epsilon/4\pi d\psi(x)/dx|_{x=a/2}$ is the electrode charge density. Then, by combining eqs 10, 11, 12, and 13, it is easy to find that the full analytic expressions for $g_{\text{diff}}(x)$, $g_{\text{sum}}(x)$, and $g_+(x)g_-(x)$ at contact, $x = a/2$, are

$$g_{\text{diff}}(a/2) = \frac{1}{\rho^*} \sqrt{\left[1 - \exp\left(-\frac{b^2}{2}\rho^*\right)\right] \times \left[1 + (2\rho^* - 1)\exp\left(-\frac{b^2}{2}\rho^*\right)\right]} \quad (14)$$

$$g_{\text{sum}}(a/2) = \frac{1}{\rho^*} \left[1 + (\rho^* - 1)\exp\left(-\frac{b^2}{2}\rho^*\right)\right] \quad (15)$$

and

$$g_-(a/2)g_+(a/2) = \exp(-b^2\rho^*) \quad (16)$$

Equations 14, 15, and 16 are the *main results* of this paper.

It should be pointed out that there are two different limit orders for eqs 14, 15, and 16 in a mathematical aspect. One is that if $\rho^* \rightarrow 0$ then $b \rightarrow \infty$. The other is that if $b \rightarrow \infty$, then $\rho^* \rightarrow 0$. However, only $\rho^* \rightarrow 0$ and then $b \rightarrow \infty$ are physically sound. This is because ρ^* is an internal parameter of the system, while b is an external parameter. As $\rho^* \rightarrow 0$, eqs 14, 15, and 16 are reduced to the following equations:

$$\lim_{\rho^* \rightarrow 0} g_{\text{diff}}(a/2) = b \sqrt{1 + \frac{b^2}{4}} \quad (17)$$

$$\lim_{\rho^* \rightarrow 0} g_{\text{sum}}(a/2) = 1 + \frac{b^2}{2} \quad (18)$$

and

$$\lim_{\rho^* \rightarrow 0} g_-(a/2)g_+(a/2) = 1 \quad (19)$$

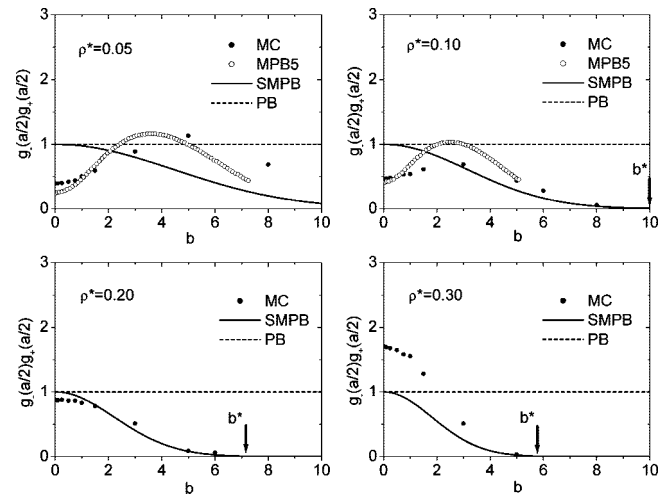


Figure 1. The contact value of the product profile $g_-(a/2)g_+(a/2)$ as a function of b at indicated values of the reduced density ρ^* . The filled symbol represents the MC data,⁷ the open circle symbol represents the numerical results of MPB5,⁷ the solid line is an analytic expression of the SMPB theory (eq 16), and the dashed line is an analytic expression of the PB theory (eq 19). The arrow indicates the value of the parameter b^* , after which the excluded volume effects dominate.

These are the full expressions of the PB theory for $g_{\text{diff}}(x)$, $g_{\text{sum}}(x)$, and $g_-(x)g_+(x)$ at contact.³

Results and Discussion

In recent MC simulations, Bhuiyan et al.⁷ simulated $g_i(x)$ using the reduced temperature $T^* = \epsilon a k_B T / (ze)^2 = 0.15$. The simulations were performed in a canonical ensemble using the standard Metropolis algorithm. The techniques that they adopted were similar to those used in the simulations by Boda et al.²⁵ and Lamperski and Bhuiyan.²⁶ They employed the Torrie–Valleau²⁷ parallel charged sheets procedure to account for the long-range Coulomb interactions. In practice, the bulk electrolyte concentration is not known a priori. They overcome it by slight adjustments to the length (perpendicular to the wall) of the central MC box.²⁸ The number of particles simulated depended essentially on the bulk concentration and varied from about 140 (which corresponds to $\rho^* = 0.02$) to about 800 (which corresponds to $\rho^* = 0.3$). The results of the MC simulations of Bhuiyan et al.⁷ are shown in Figure 1 for $g_-(a/2)g_+(a/2)$ by the filled symbol. They found that⁷

$$\lim_{b \rightarrow +\infty} g_-(a/2)g_+(a/2) \rightarrow 0 \quad (20)$$

and they pointed out that $g_-(a/2)g_+(a/2)$ can exhibit a nontrivial behavior.

The analytical results of the SMPB theory, as well as of the PB theory, for $g_-(a/2)g_+(a/2)$ vs b at different reduced densities, which are given by eqs 16 and 19, are compared with the corresponding MC data⁷ in Figure 1. It is clearly seen that $g_-(a/2)g_+(a/2)$ drops to zero as $b \rightarrow +\infty$, while it is unity from the PB theory (eq 19). Moreover, as ρ^* increases, the speed that $g_-(a/2)g_+(a/2)$ drops to zero increases, which reveals that $g_-(a/2)g_+(a/2) \rightarrow 0$ originates from the steric effect. However, it fails to reproduce the MC data⁷ at small b . It is worth addressing that, in the previous study,⁷ the

numerical results calculated by a plethora of modified Poisson–Boltzmann equations perturbing PB theory (which is called MPB5 and in which the excluded volume term has been evaluated via an inhomogeneous Ornstein–Zernike equation)^{28,29} have been used for comparison with the MC data.⁷ Due to the limitations of the numerical technique that was used, except for very small b , no convergent solutions of the MPB5 equation could be obtained for $\rho^* = 0.2$ and 0.3 ; i.e., there are no numerical results of MPB5 for $\rho^* = 0.2$ and 0.3 . The numerical results of MPB5 for $\rho^* = 0.05$ and 0.1 , which were obtained by Bhuiyan et al.,⁷ are shown in Figure 1. It can be seen that at small b , the numerical results of the MPB5 are in better agreement with the MC results than the analytical expression of the SMPB theory. This is because the MPB5 includes the fluctuation effects, while the SMPB theory is mean field like. The reason that the analytic expression of the SMPB theory fails to reproduce the MC data⁷ at small b can be traced to the neglect of fluctuation effects, which implies that there are remarkable ionic correlations in that regions; i.e., the correlated fluctuations of ion distributions cannot be omitted.⁷

On the other hand, at large b , due to the scarcity of the numerical results of MPB5, it is impossible here to compare the analytic expression of the SMPB theory with the numerical results of MPB5, which is an interesting topic that is worth investigating further. It is noted that we define the parameter b^* , after which the excluded volume effects dominate, such that for $\rho^* = 0.1$ the parameter $b^* = 10$ (shown in Figure 1b by the arrow); from eq 16, we find that b^* satisfies the equation $b^* = (10.0/\rho^*)^{1/2}$. Then, we deduce that $b^* = 14.14$ for $\rho^* = 0.05$, $b^* = 7.07$ for $\rho^* = 0.2$, and $b^* = 5.77$ for $\rho^* = 0.3$ (shown in Figure 1c,d by the arrow, respectively, while for $\rho^* = 0.05$, $b^* = 14.14$ is beyond the range of b shown in Figure 1a), which are in quite good agreement with the MC results.

It is worth pointing out that for a system with $T^* = 0.15$, the Coulombic interaction is strong and correlation and fluctuation effects would be important, which are shown by the behavior of the system at small b . On the other hand, when b is large, a mean field approach can capture the behavior of the system. Note that b is the dimensionless electrode charge density. Larger b means larger external electric field. Thus, we can get the following information: (1) as b increases, the Coulombic interaction, correlation, and fluctuation effects will be restrained by the larger external electric field; (2) the product vanishes at high charge density because of the density saturation of the ionic layer rather than the correlation and fluctuation effects. Therefore, we can conclude that the behavior of $g_{-}(a/2)g_{+}(a/2)$ may be controlled mainly by two factors. One is the ionic correlation effect, which controls the behavior of $g_{-}(a/2)g_{+}(a/2)$ at small b . The other is the steric effect that is captured by the analytic expression of the SMPB theory, which leads to $g_{-}(a/2)g_{+}(a/2) \rightarrow 0$ as $b \rightarrow +\infty$.

More recently, Bhuiyan and Henderson³⁰ examined $g_{\text{diff}}(a/2)$ by using the extensive simulation results of Bhuiyan et al.⁷ The data of Bhuiyan and Henderson³⁰ and the corresponding analytical results given by eqs 14 (the SMPB theory) and 17 (the PB theory) are shown in Figure 2. It is clearly seen

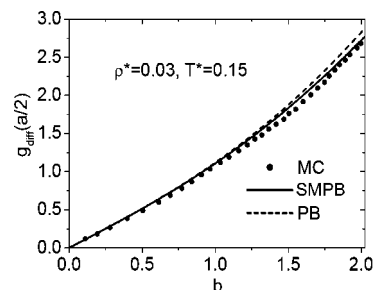


Figure 2. The contact value of the difference profile $g_{\text{diff}}(a/2)$ as a function of b at reduced density $\rho^* = 0.03$ and reduced temperature $T^* = 0.15$. The filled symbol represents the MC data,³⁰ the solid line is an analytic expression of the SMPB theory (eq 14), and the dashed line is an analytic expression of the PB theory (eq 17).

that, at small b , both analytic expressions of eqs 14 and 17 reproduce the data of Bhuiyan and Henderson³⁰ remarkably well. However, as b increases, the result of the PB theory departs from the data, but the analytical expression of the SMPB theory still reproduces the data quite well, which shows again the importance of including steric effects in modeling diffuse layer properties.

Conclusions

In conclusion, we have obtained the exact analytic expressions for the contact values in the SMPB theory. In particular, we have shown that the exact analytic expression allows us to account for the following behaviors of the contact product that are displayed by the MC simulation:⁷ (i) $g_{-}(a/2)g_{+}(a/2)$ tends to zero as $b \rightarrow +\infty$; (ii) the speed that $g_{-}(a/2)g_{+}(a/2)$ drops to zero increases with increasing ρ^* . In addition, for $g_{\text{diff}}(a/2)$, the analytical expression of the SMPB theory also reproduces the data of Bhuiyan and Henderson³⁰ quite well. In contrast, the popular PB theory does not reproduce a vanishing contact value of the product profile at large b . Moreover, only at low ρ^* and small b region does the PB theory reproduce the data of Bhuiyan and Henderson³⁰ for $g_{\text{diff}}(a/2)$. As b increases, the result of the PB theory departs from the MC data. The present study demonstrates that the SMPB theory can give a quick, qualitative insight into the effects of a finite ion size and is worth investigating further.

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Appendix

Derivation of Eqs 14, 15, and 16 Using the boundary conditions $\psi(x)|_{x=a/2} = \psi(a/2)$, $\psi(x)|_{x \rightarrow \infty} = 0$, and $d\psi(x)/dx|_{x \rightarrow \infty} = 0$, at contact, $x = a/2$, we can get the difference, sum, and product profiles as

$$g_{\text{diff}}(a/2) = \frac{\sinh(z\epsilon\beta\psi(a/2))}{1 + 2\rho^* \sinh^2\left(\frac{z\epsilon\beta\psi(a/2)}{2}\right)} \quad (\text{A1})$$

$$g_{\text{sum}}(a/2) = \frac{\cosh(ze\beta\psi(a/2))}{1 + 2\rho^* \sinh^2\left(\frac{ze\beta\psi(a/2)}{2}\right)} \quad (\text{A2})$$

and

$$g_{-}(a/2)g_{+}(a/2) = \frac{1}{\left[1 + 2\rho^* \sinh^2\left(\frac{ze\beta\psi(a/2)}{2}\right)\right]^2} \quad (\text{A3})$$

On the other hand, for the electrode charge density ($\sigma = -\epsilon/4\pi \, d\psi(x)/dx|_{x=a/2}$)

$$\sigma = -\sqrt{\frac{c_b\epsilon}{\pi\beta\rho^*}} \sqrt{\ln\left[1 + 2\rho^* \sinh^2\left(\frac{ze\beta\psi(a/2)}{2}\right)\right]} \quad (\text{A4})$$

Equation A4 can be rewritten as

$$\frac{b^2}{2}\rho^* = \ln\left[1 + 2\rho^* \sinh^2\left(\frac{ze\beta\psi(a/2)}{2}\right)\right] \quad (\text{A5})$$

then

$$1 + 2\rho^* \sinh^2\left(\frac{ze\beta\psi(a/2)}{2}\right) = \exp\left(\frac{b^2}{2}\rho^*\right) \quad (\text{A6})$$

and

$$\sinh^2\left(\frac{ze\beta\psi(a/2)}{2}\right) = \frac{1}{2\rho^*} \left[\exp\left(\frac{b^2}{2}\rho^*\right) - 1 \right] \quad (\text{A7})$$

where $b = 2\pi\beta\sigma^2/c_b\epsilon$.

Using the following formulas

$$\sinh(A) = 2 \sinh\left(\frac{A}{2}\right) \sqrt{1 + \sinh^2\left(\frac{A}{2}\right)}$$

$$\cosh(A) = 1 + 2 \sinh^2\left(\frac{A}{2}\right)$$

and eq A7, we can get

$$\sinh(ze\beta\psi(a/2)) = \frac{\exp\left(\frac{b^2}{2}\rho^*\right)}{\rho^*} \sqrt{\left[1 - \exp\left(-\frac{b^2}{2}\rho^*\right)\right]} \times \sqrt{\left[1 + (2\rho^* - 1)\exp\left(-\frac{b^2}{2}\rho^*\right)\right]} \quad (\text{A8})$$

and

$$\cosh(ze\beta\psi(a/2)) = \frac{\exp\left(\frac{b^2}{2}\rho^*\right)}{\rho^*} \left[1 + (\rho^* - 1)\exp\left(-\frac{b^2}{2}\rho^*\right)\right] \quad (\text{A9})$$

Substituting eqs A6, A8, and A9 into eqs A1, A2, and A3, we have

$$g_{\text{diff}}(a/2) = \frac{1}{\rho^*} \sqrt{\left[1 - \exp\left(-\frac{b^2}{2}\rho^*\right)\right]} \times \sqrt{\left[1 + (2\rho^* - 1)\exp\left(-\frac{b^2}{2}\rho^*\right)\right]} \quad (\text{A10})$$

$$g_{\text{sum}}(a/2) = \frac{1}{\rho^*} \left[1 + (\rho^* - 1)\exp\left(-\frac{b^2}{2}\rho^*\right)\right] \quad (\text{A11})$$

and

$$g_{-}(a/2)g_{+}(a/2) = \exp(-b^2\rho^*) \quad (\text{A12})$$

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