Ionic Distribution, Electrostatic Potential and Zeta Potential at Electrochemical Interfaces*

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Abstract Density functional theory is applied to predicting the structures and electrostatic potentials of planar electrochemical surfaces within the framework of the restricted primitive model where small ions are represented by charged hard spheres of equal diameter and the solvent is assumed to be a continuous dielectric medium. The hard-sphere contribution to the excess Helmholtz energy functional is evaluated using the modified fundamental-measure theory and the electrostatic contribution is obtained from the quadratic functional Taylor expansion using the second-order direct correlation function from the mean-spherical approximation. Numerical results for the ionic density profiles and the mean electrostatic potentials near a planar surface of various charge densities are in excellent agreement with molecular simulations. In contrast to the modified Gouy-Chapman theory, the present density functional theory correctly predicts the second layer formation and charge inversion of charged surfaces as observed in simulations and in experiments. The theory has also been tested with the zeta potentials of positively charged polystyrene particles in aqueous solutions of KBr. Good agreement is achieved between the calculated and experimental results.

Keywords density functional theory, electric double layer, zeta potential, polystyrene colloid

1 INTRODUCTION

An electric double layer (EDL) is the surface of a metal electrode or a charged particle together with a layer of counterions neutralizing the surface charge. The structure of EDL has been of particular interest to electrochemists, biochemists and chemical engineers for many years. Most electrochemical reactions take place within the EDL, the stability of a charge-stabilized colloidal dispersion crucially depends on the distribution of small ions in the EDL, and the transport properties of cell membranes are determined in part by the charge distribution in the EDL. A quantitative understanding of the structure of EDL is important for controlling the stability of disperse systems, designing electrokinetic processes, and desalting of liquid on organic membranes and many biological systems\cite{1,2}.

The classical and yet the most widely used theory for EDL is the modified Gouy-Chapman (MGC) theory\cite{3}. It is assumed that the short-ranged repulsion between small ions and the correlations of their density distributions in EDL are negligible and the charged surface can be represented by a rigid boundary. Because of the negligence of ionic correlations, the MGC theory is unable to describe interesting electrostatic phenomena recently discovered by experiments and simulations such as counterion layering, charge inversion, and attraction between like charges. The restricted primitive model (RPM) represents the first step toward the improvement of the MGC theory. In the RPM, all the small ions are represented by charged hard spheres of equal diameter, the charged surface is regarded as a uniformly charged planar wall, and the solvent remains as a continuous dielectric medium. Within the framework of the RPM, the ionic distributions in EDL have been extensively investigated by molecular simulation methods and various theoretical approaches including modified Poisson-Boltzmann (MPB) theory\cite{5}, integral equation (IE) theory\cite{6}, and density functional theory (DFT)\cite{18, 19}. The details of these theoretical methods on the structure of EDL have been compared by Carnie and Torrie\cite{10}. All previous theoretical approaches, including the highly-sophisticated hybrid hypernetworked chain (HNC)/mean spherical approximation (MSA) theory where the wall-ion correlations are described by the HNC theory and the ion-ion correlations by the MSA theory, are unable to predict multiple layering of counterions\cite{11}. The purpose of present work is to develop a new version of DFT for representing the structure of nonuniform ionic fluids that is able to capture the novel electrostatic phenomena.

Various versions of DFT for describing the structures of EDLs have been recently reviewed by Hansen and Loven\cite{12}. Most previous works follow a perturbation approach where the excess Helmholtz energy due to the hard-sphere repulsion is given by a weight-
density approximation (e.g. Tarazona recipe) and that due to the electrostatic interactions is taken into account by a quadratic expansion with respect to that for a uniform fluid of known direct correlation functions. In particular, Boda et al. used the generalized MSA (GMSA) to describe the properties of the uniform bulk fluids in order to improve the performance of DFT for systems containing strongly coupled ions. Unlike other approaches, this improvement correctly captures the drying of the planar electrode. Previous applications of DFT for the planar EDLs indicate that for systems containing monovalent counterions, DFT, MPB and HNC/HNC theories yield comparable results. However, DFT is significantly more accurate than alternative approaches in the presence of multivalent counterions or in mixed electrolyte solutions.

This paper presents a partially perturbative DFT for representing the ionic density distributions and electrostatic potentials of planar charged surfaces within the restrictive-primitive-model for electrolyte solutions. The excess free energy functional due to hard sphere repulsion is evaluated through an improved fundamental measure theory and the electrical contribution is calculated using a quadratic expansion with respect to that for the uniform fluid. The DFT is applied to investigating the effect of surface charge density and electrolyte concentration on the mean electrostatic potential, the structure of planar EDL, and the layer formation of counterions. We compare the results from the DFT with Monte Carlo simulation data and the predictions of the MGC theory. To test its applicability for practical systems, the DFT is also used to calculate the ζ potential of positively charged latex particles in aqueous KBr solutions and the results are compared with experimental data.

2 THEORY
2.1 The primitive model of planar EDL
In the primitive model of electrolyte solutions, all the small ions are represented by charged hard spheres, the solvent is considered as a continuum with a dielectric constant ε, and a charged surface is regarded as a rigid wall. The pair potential between small ions is given by

\[ u_{ij}(r) = \begin{cases} \infty & r < \sigma_{ij} \\
\frac{z_i z_j e^2}{\varepsilon r} & r > \sigma_{ij} \end{cases} \]

where σ_{ij} and z_{i}e are, respectively, the diameter and charge of ith ion, \(\sigma_{ij} = (\sigma_i + \sigma_j)/2\), and the external potential acting on the ith ion due to the charged wall is given by

\[ V_{\text{ext}}(r) = \begin{cases} \infty & z < \sigma_i/2 \\
-\frac{z_i e E z}{\varepsilon} & z > \sigma_i/2 \end{cases} \]

where \(E/4\pi = Q\) is the surface charge density on the wall and \(z\) is the perpendicular distance from the wall. In the restricted primitive model (RPM), all the small ions have the same diameter.

The mean electrostatic potential \(\psi(z)\) due to the uniform surface charge density \(Q\) at the wall and diffusive small ions satisfies the Poisson equation

\[ \psi(z) = \frac{4\pi}{\varepsilon} \int_{-\infty}^{\infty} dz' (z - z') \sum_i z_i e \rho_i(z') \]

(3)

The electroneutrality condition of the system is given by

\[ \int_{-\infty}^{\infty} dz' \sum_i z_i e \rho_i(z') + Q = 0 \]

(4)

With an appropriate closure as given by the Poisson-Boltzmann equation or a density functional theory, both \(\psi(z)\) and the density profiles can be iteratively solved from Eqs. (2) and (3).

2.2 Density functional theory
The grand potential for ions with chemical potential \(\mu_i\) in an external potential of \(V_{\text{ext}}(r)\) is related to the Helmholtz energy functional through the Legendre transform

\[ \Omega[\{\rho_i\}] = F[\{\rho_i\}] + \sum_{i=1}^{N} \int \text{d}r [V_{\text{ext}}(r) - \mu_i] \rho_i(r) \]

(5)

where \(\{\rho_i\}\) is a set of density distributions for all small ions, \(N\) is the total number of ionic species, and \(F[\{\rho_i\}]\) represents the Helmholtz energy functional. At equilibrium, the grand potential reaches a minimum, yielding the Euler-Lagrange equation for solving the density distributions

\[ \mu_i - V_{\text{ext}}(r) = \sigma F'[\{\rho_i\}] / \sigma \rho_i(r) \]

(6)

The key problem in a density functional theory is to formulate an analytical expression for the Helmholtz energy \(F\) as a function of the density distributions. Without the loss of generality, we may decompose \(F\) into four parts, i.e.,

\[ F[\{\rho_i\}] = F_{\text{id}}[\{\rho_i\}] + F_{\text{hs}}[\{\rho_i\}] + F_{\text{C}}[\{\rho_i\}] + F_{\text{el}}[\{\rho_i\}] \]

(7)

where \(F_{\text{id}}\) is the ideal-gas contribution, \(F_{\text{hs}}\) is the hard-sphere contribution, \(F_{\text{C}}\) is the direct Coulomb contribution, and \(F_{\text{el}}\) represents a coupling of Coulombic and hard-sphere interactions. The ideal-gas contribution is given by the exact expression

\[ F_{\text{id}}[\{\rho_i\}] = k_b T \sum_{i=1}^{N} \int \text{d}r \rho_i(r) [\ln(\rho_i(r) \lambda_i^3) - 1] \]

(8)
where $\lambda_i$ is the thermal de Broglie wavelength of component $i$ and $k_B$ is the Boltzmann constant. The direct Coulomb contribution is also known exactly, given by

$$F^{\text{ex}}_{\text{ex}}[\{\rho_i\}] = \frac{1}{2} \int dr_1 dr_2 \sum_{i,j} z_i z_j e^2 \rho_i(r_1) \rho_j(r_2) \delta(r_1 - r_2)$$

(9)

To find expressions for $F^{\text{ex}}_{\text{ex}}[\{\rho_i\}]$ and $F^{\text{ex}}_{\text{el}}[\{\rho_i\}]$ (both are ignored in the MGC theory), we use a recently-developed modified fundamental measure theory (MFMT)\cite{15,16} for short-ranged repulsions and a quadratic expansion of the Helmholtz energy function\cite{8} for electrostatic interactions. According to MFMT, $F^{\text{ex}}_{\text{ex}}[\{\rho_i\}]$ is given by

$$\beta F^{\text{ex}}_{\text{ex}} = \int \phi^{\text{hs}}[n_{\alpha}(r)] dr$$

(10)

where $\beta = 1/k_B T$, $n_{\alpha}(r)$ is the weighted density, and $\phi^{\text{hs}}[n_{\alpha}(r)]$ is the reduced excess Helmholtz energy density due to hard-sphere repulsion. Following Rosenfeld's original work, the hard-sphere Helmholtz energy density can be expressed as \cite{16}

$$\phi^{\text{hs}}[n_{\alpha}(r)] = \phi^{\text{hs}(S)}[n_{\alpha}(r)] + \phi^{\text{hs}(V)}[n_{\alpha}(r)]$$

(11)

where the superscripts "S" and "V" stand for contributions from scalar and vector weighted densities, respectively. The scalar part according to MFMT\cite{16} is given by

$$\phi^{\text{hs}(S)}[n_{\alpha}(r)] = -n_0 \ln(1 - n_3) + \frac{n_1 n_2}{1 - n_3} + \frac{n_3^2}{36\pi n_3^2} \ln(1 - n_3)$$

$$+ \frac{n_3^2}{36\pi n_3^2} \ln(1 - n_3)$$

$$+ \frac{n_3^2}{36\pi n_3^2} \ln(1 - n_3)$$

(12)

and the vector part is given by

$$\phi^{\text{hs}(V)}[n_{\alpha}(r)] = -n_{V1} \cdot n_{V2} +$$

$$-n_2 n_{V2} \cdot n_{V2}$$

$$12\pi n_3^2 \ln(1 - n_3)$$

$$- \frac{n_2 n_{V2} \cdot n_{V2}}{12\pi n_3^2}$$

$$+ \frac{n_2 n_{V2} \cdot n_{V2}}{12\pi n_3^2}$$

(13)

In the limit of a bulk fluid, the two vector weighted densities $n_{V1}$ and $n_{V2}$ vanish, and the Helmholtz free energy density $\phi^{\text{hs}}$ becomes identical to that from the Boublik-Mansoori-Carnahan-Starling-Leland (BMCSL) equation of state\cite{16}.

As in Rosenfeld’s original FMT\cite{15,16}, the weighted densities in Eqs. (12) and (13) are defined as

$$n_{\alpha}(r) = \sum_{i=1}^{N} n_{\alpha i}(r) = \sum_{i=1}^{N} \int \rho_i(r') w^{(\alpha)}_i(|r' - r|) dr'$$

(14)

where the subscripts $\alpha = 0, 1, 2, 3$, V1 and V2 denote the index of six weight functions $w^{(\alpha)}_i(r)$ that characterize the volume, surface area and surface vector averages of a spherical particle $i$. The six weight functions are independent of the density profiles. Among them, three weight functions are directly related to the geometry of a spherical particle $i$, namely particle size, surface area and volume,

$$w_i^{(0)}(r) = \delta(\sigma_i/2 - r)$$

$$w_i^{(1)}(r) = \theta(\sigma_i/2 - r)$$

$$w_i^{(2)}(r) = (r/\sigma_i)^{2} \delta(\sigma_i/2 - r)$$

(15) (16) (17)

where $\delta(r)$ is the Dirac delta function and $\theta(r)$ is the Heaviside step function. Integration of two scalar weight functions, $w_i^{(0)}(r)$ and $w_i^{(1)}(r)$, with respect to the position gives the particle surface area and volume, respectively, and integration of the vector weight function, $w_i^{(2)}(r)$, is related to the gradient across the sphere in the $r$ direction. Other weight functions are proportional to the three functions given in Eqs. (15)---(17), i.e.,

$$w_i^{(V1)}(r) = \frac{w_i^{(V2)}(r)}{2\pi\sigma_i^2}$$

(19)

Following the previous applications of DFT for electric double layers, we derive $F^{\text{ex}}_{\text{ex}}[\{\rho_i\}]$ by a functional Taylor expansion of the residual Helmholtz free energy functional around that of a uniform fluid

$$F^{\text{ex}}_{\text{el}}[\{\rho_i\}] = F^{\text{ex}}_{\text{el}}[\{\rho_i^0\}] + \int dr \sum_{i=1}^{N} \delta F^{\text{ex}}_{\text{el}}(\rho_i(r)) +$$

$$\frac{1}{2} \int dr dr' \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\delta^2 F^{\text{ex}}_{\text{el}}}{\delta \rho_i(r) \delta \rho_j(r')} \Delta \rho_i(r) \Delta \rho_j(r')$$

(20)

where $\{\rho_i^0\}$ is the set of all bulk densities and $\Delta \rho_i(r) = \rho_i(r) - \rho_i^0$. According to the definition of the direct correlation functions and neglecting all higher-order terms $\Delta C^{(n)}_{ij} (n > 2)$ in Eq. (20), $F^{\text{ex}}_{\text{el}}[\{\rho_i\}]$ becomes

$$\beta F^{\text{ex}}_{\text{el}}[\{\rho_i\}] = \beta F^{\text{ex}}_{\text{el}}[\{\rho_i^0\}] - \int dr \sum_{i=1}^{N} \Delta C^{(1)}_{i} \Delta \rho_i(r) +$$

$$\frac{1}{2} \int dr dr' \sum_{i=1}^{N} \sum_{j=1}^{N} \Delta C^{(2)}_{ij} (|r' - r|) \Delta \rho_i(r) \Delta \rho_j(r')$$

(21)

where the excess direct correlation function $\Delta C^{(2)}_{ij}(r)$ is defined as

$$\Delta C^{(2)}_{ij}(r) = C_{ij}(r) + \frac{\beta z_i z_j e^2}{\varepsilon r} - C^{\text{hs}}_{ij}(r)$$

(22)

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\( \Delta C_{ij}^{(2)el}(r) \) can be obtained from, for example, numerical solutions of HNC or hybridized MSA closure of the OZ equation. A popular approach to calculate \( \Delta C_{ij}^{(2)el}(r) \) is from the mean-spherical approximation (MSA) that gives analytical expressions of direct correlation functions and thermodynamic properties of simple electrolyte solutions in reasonable accuracy\(^{19}\). In restrictive primitive model, \( \Delta C_{ij}^{(2)el}(r) \) according to MSA is given by

\[
\Delta C_{ij}^{(2)el}(r) = \begin{cases} 
\frac{z_i z_j e^2 \beta}{\varepsilon} \left[ \frac{2B}{\sigma} - \left( \frac{B}{\sigma} \right)^2 \frac{r - 1}{r} \right] & r < \sigma \\
0 & r > \sigma 
\end{cases}
\]

where

\[
B = \Gamma \sigma / (1 + \Gamma \sigma)
\]

and \( \Gamma \) is related to the inverse of the Debye screening length

\[
\kappa^2 = \frac{4\pi \beta e^2}{\varepsilon} \sum_{i=1}^{N} \rho_i^b z_i^2
\]

by

\[
\kappa = 2\Gamma (1 + \Gamma \sigma)
\]

Substituting Eqs. (7)–(10) and (21) into Eq. (6) and considering planar geometry, we obtain the explicit Euler-Lagrange equation for the density profiles of ions in planar EDL

\[
-kT \ln \left( \frac{\rho_i(z)}{\rho_i^0} \right) = \left[ \frac{\delta F_{hs}^{ex}}{\delta \rho_i(z')} - \mu_i^{ex} \right] + z_i e \psi(z) - kT \sum_{j=1}^{N} \int dz' \Delta C_{ij}^{(2)el}(|r' - r|) \Delta \rho_j(z')
\]

where \( F_{hs}^{ex} \) is evaluated from Eq. (10) and \( \psi(z) \) from Eq. (3). Eq. (27) can be solved numerically to obtain the ionic density profiles and subsequently electrostatic potentials.

2.3 Numerical details

The weighted densities and the integrals are evaluated using a trapezoidal mesh with a uniform mesh \((\Delta x = 0.01 \sigma)\) that yields satisfactory numerical accuracy. At each step, the electroneutrality condition is applied and the iteration continues until a specified convergence is reached. For comparison between the predicted results and molecular simulation data, the parameters used in the calculation are identical to those used in the simulations. In most examples shown in this work, the diameter of small ions is \( \sigma = 0.3 \text{ nm} \) or \( \sigma = 0.425 \text{ nm} \). The dimensionless quantities are defined as \( T^* = e^2 \kappa T^2 / \varepsilon^2 \), \( z^* = z / \sigma \), \( Q^* = Q \sigma^2 / \varepsilon \) and \( \psi^*(z) = e \psi(z) / kT \).

3 RESULTS AND DISCUSSION

3.1 Ion density profiles

We first consider the ionic density profiles near a surface of various charge densities in a 1:1 electrolyte solution with the concentration \( c = 1.0 \text{ mol} \cdot \text{L}^{-1} \). Figs. 1–3 show the calculated results for three surface charge densities \( \psi^* = 0.1685, 0.55 \text{ and } 0.7 \), respectively. At low surface charge density (see Fig. 1), the DFT predicts monotonic density profiles of counterions and coions, in good agreement with the Monte Carlo simulation data\(^{19}\). As expected, there is a significant accumulation of counterions near the charged wall, accompanied by a depletion of coions in the same region. For monovalent counterions up to moderate surface charges, the diffuse layer falls off gradually and extends a few molecular diameters into the solution.

But as the surface charge density is further increased (see Figs. 2 and 3), the density profiles of counterions predicted from the present DFT become non-monotonic and show interesting counterion layering. As depicted in Figs. 2 and 3, the second counterion layering becomes more pronounced as the surface charged density increases. All previous theoretical approaches fail to capture the subtle formation of the second counterion layers.
and small ions. A surface with high surface charge density attracts substantial counterions in the EDL but the steric effects and inter-ionic correlations preclude distant counterions from drifting to near the charged wall. These counterions then pack themselves into a second layer at next nearest optimum distance (around 1.5σ) from the charged wall[21]. In addition, the increased surface charge density on the charged hard wall also causes an excessive accumulation of counterions near the wall, accompanied by an excessive depletion of coions. The predictions of the layering effects from the present DFT for high surface charge densities agree quantitatively with the MC simulations[6,20] for the planar EDL. In contrast, since the excluded volume is neglected, the MGC theory is unable to predict the counterion layering phenomena.

![Figure 3](image)

**Figure 3** Ionic density profiles near a charged surface in a 1:1 electrolyte solution

\begin{align*}
\rho_1(z)/\rho_\infty &= 0.425 \text{ nm}, c = 1.0 \text{ mol}\cdot\text{L}^{-1}, \\
Q^* &= 0.70, T^* = 0.59495
\end{align*}

- MC for counterion; \(\Delta\) MC for coion; 
- present DFT; \(-\cdots\) MGC

At higher concentrations of electrolytes, the DFT predicts marked oscillations in the ionic density profiles. Fig. 4 shows the ionic density distributions calculated from the DFT, MGC and Monte Carlo simulations for a 2.0 mol\cdot\text{L}^{-1} electrolyte solution near a charged wall with \(Q^* = 0.396\). The DFT correctly reproduces the oscillation of ionic density profiles for both counterions and coions near the wall. The crossover point on the ion density profiles of the counterions and the coions suggests a charge inversion phenomenon, where counterions are accumulated too much near the wall such that the overall charge has opposite sign of the bare charge. In Fig. 4, we also plot the result of the DFT without \(F_{\text{ex}}\) term, i.e., \(F_{\text{ex}} = 0\). In this case, there is on crossover point on the ionic density profiles of the counterion and coion but a second layering. It can be concluded that \(F_{\text{ex}}\) term is related to the interesting charge inversion phenomena, while the second layering effect is due to hard sphere term \(F_{\text{hs}}\). If we neglect both \(F_{\text{ex}}\) and \(F_{\text{hs}}\) terms, the present DFT reduces to the MGC theory, which is unable to predict the oscillations in the ionic density distributions and the interesting charge inversion phenomena, as can be seen from Figs. 1—4.

![Figure 4](image)

**Figure 4** Ionic density profiles near a charged surface in a 1:1 electrolyte solution

\(\sigma = 0.425 \text{ nm}, c = 2.0 \text{ mol}\cdot\text{L}^{-1}, \\
Q^* = 0.396, T^* = 0.59495\)

- MC for counterion; \(\Delta\) MC for coion; 
- present DFT; \(-\cdots\) MGC; \(\cdots\cdots\) DFT without \(F_{\text{ex}}\) term

For a 2:1 electrolyte near a wall with positive charge density (counterion is still monovalent), the ion density profiles[4] as shown in Fig. 5 is similar to that for a 1:1 electrode at low surface charge density. As found by others, a comparison of Figs. 1 and 5 indicates that the structure of the EDL is mainly determined by the counterions. In other words, coions have little effect on the ionic distributions in the EDL.

![Figure 5](image)

**Figure 5** Ionic density profiles near a charged surface in a 2:1 electrolyte solution

\(\sigma = 0.425 \text{ nm}, c = 0.5 \text{ mol}\cdot\text{L}^{-1}, Q^* = 0.2, T^* = 0.59495\)

- MC for counterion; \(\Delta\) MC for coion; 
- present DFT; \(-\cdots\) MGC

In the present DFT, the contributions of the ideal gas, the direct Coulomb and the coupling of Coulombic and hard-sphere interactions to the Helmholtz energy functional are the same as that in the previous versions[8,9,13]. However, the more accurate \(F_{\text{ex}}\) term[16,17] is used in this work. Therefore, the present DFT at least is slightly better than the previous DFTs.

### 3.2 Electrostatic potential

Figures 6 and 7 present the distributions of mean electrostatic potentials in the systems as shown in Figs. 1 and 5, respectively. In comparison with simulations, the MGC theory overestimates \(\psi^*(z)\) because it neglects the ionic correlation. In Fig. 6, \(\psi^*(z)\) changes sign near 1.5σ, suggesting also the charge inversion...
as discussed earlier. Apparently, this subtle feature is captured by the present DFT.

Figure 6 Mean electrostatic potential near a charged surface in a 1:1 electrolyte solution
\[ \sigma = 0.425 \text{ nm}, c = 2.0 \text{ mol-L}^{-1}, Q^* = 0.286, T^* = 0.59495 \]
\[ \Delta \text{ MC data; } \text{--- present DFT; } \cdots \cdots \text{ MGC} \]

Figure 7 Mean electrostatic potential near a charged surface in a 2:1 electrolyte solution
\[ \sigma = 0.425 \text{ nm}, c = 0.5 \text{ mol-L}^{-1}, Q^* = 0.2, T^* = 0.59495 \]
\[ \Delta \text{ MC data; } \text{--- present DFT; } \cdots \cdots \text{ MGC} \]

The diffuse layer potential, \( \psi^*(\sigma/2) \), corresponds to the mean-electrostatic potential at the contact of small ions and the rigid surface. In Fig. 8, we plot the diffuse layer potential as a function of surface charge density. It shows that at both high and low electrolyte concentrations (1.0 mol-L\(^{-1}\) and 0.10 mol-L\(^{-1}\)), the MGC overestimates the diffuse layer potential and it becomes more pronounced as the surface charge density increases. That can be explained by the fact that the MGC theory neglects excluded-volume effect and the correlations of ionic distributions. In contrast, the diffuse layer potentials predicted from the present DFT are in excellent agreement with the Monte Carlo simulation results\[^3\] up to moderate surface charge densities. At higher surface charge densities, the present DFT slightly underestimates the diffuse layer potential at both 1.0 mol-L\(^{-1}\) and 0.10 mol-L\(^{-1}\).

3.3 Zeta potential of polystyrene colloid

We have also tested the performance of the DFT by using \( \zeta \) potentials obtained from electrophoretic mobility experiments for positively charged polystyrene colloids. Upon the application of an external electric field, a charged particle in an electrolyte solution moves towards the electrodes and the mobility is directly related to the overall charge of the colloidal particle, i.e., the bare charge plus the charges of adsorbed counterions. The \( \zeta \) potential refers to the mean electrostatic potential at the slipping plane between the particle and the surrounding solution. Moleon-Baca et al.\[^{21}\] reported the \( \zeta \) potential of positively charged polystyrene colloids (sample K8 and K9) in various KBr aqueous solutions at pH=6.1 and \( T = 298 \text{ K} \). These monodispersed latex particles were prepared by emulsifier-free emulsion polymerization of styrene in the presence of azo-\( N,N' \)-dimethylene-isobutyramidine-hydrochloride at 323.15 K and pH=3.0. The diameters of the samples K8 and K9 are \( a = (630 \pm 20) \text{ nm} \) and \( a = (740 \pm 15) \text{ nm} \), respectively. Because the diameter of the latexes is much larger than that of small ions (\( a > \sigma \)), the EDL in these systems are essentially planar, i.e., the surface of colloidal particles can be represented by a planar wall. In our calculations, we use the Pauling diameter for Br\(^-\), i.e., \( \sigma = 0.390 \text{ nm} \). Because the properties of EDL are dominated by the counterions (as indicated in Section 3.1), we assume the same diameter is applicable to K\(^+\). If the latex surface is smooth and if there is no organic impurities and polyelectrolytes adsorbed on the latex surface, diffuse layer potential is a good approximation to the \( \zeta \) potential. However, the surface roughness of the charged polystyrene particles results in a larger value for the location of the shear plane\[^{22}\]. Due to the roughness of the latex surface, the shear plane seems to move further away from the latex surface as the electrophoretic radius \( \kappa_a \) decreases\[^{23}\]. In order to describe these features, we assume that the shear plane is placed at \( \sigma + \frac{10}{10} \kappa \). The surface charge densities of latex K8 and K9 according to the \( \zeta \) potential measurements are \( Q = 0.0126 \text{C-m}^{-2} \), and \( Q = 0.0116 \text{C-m}^{-2} \), respectively.

Figures 9 and 10 compare the calculated \( \zeta \) potentials of latex K8 and K9 with experimental data. In general, the results from the present DFT are in good agreement with the experimentally measured \( \zeta \) potentials. Also plotted in Figs.9 and 10 are the
diffuse layer potentials. In both cases, these potentials are larger than the \( \zeta \) potentials over the whole range of electokinetic radius \( \kappa a \). As discussed earlier, \( \psi(a/2) > \zeta \) is a consequence of the surface roughness of the latex particles, the larger value for the location of the shear plane. The smaller value for the \( \zeta \) potential. As shown in Figs. 9 and 10, the values of \( \zeta \) potential of positive charged monodisperse latexes decrease with the increase of electokinetic radius (or the concentration of KBr). This example illustrates that the present DFT can be successfully applied to calculating the \( \zeta \) potentials of polystyrene colloids in various aqueous electrolyte solutions. We did not compare the present DFT with the MGC in Figs. 9 and 10 because the concentrations of electrolyte in the two cases are so low that there is little difference between the DFT and the MGC. To demonstrate the advantage of the present DFT, experimental data for \( \zeta \) potential of colloidal particles in concentrated electrolyte solutions are required.

![Figure 9](image)

**Figure 9** The \( \zeta \) potential and diffuse potential of a latex particle (sample K8, radius \( a = 630 \text{ nm} \)) as a function of electokinetic radius \( \kappa a \) in various aqueous solutions of KBr at pH=6.1 and \( T=298 \text{ K} \)

- \( \Delta \) experimental \( \zeta \) potential;
- \( - - - - \) \( \zeta \) potential from present DFT;
- \( - - - - \) diffuse potential

![Figure 10](image)

**Figure 10** The \( \zeta \) potential and diffuse potential of a latex particle (sample K9, radius \( a = 740 \text{ nm} \)) as a function of electokinetic radius \( \kappa a \) in various aqueous solutions of KBr at pH=6.1 and \( T=298 \text{ K} \)

- \( \Delta \) experimental \( \zeta \) potential;
- \( - - - - \) \( \zeta \) potential from present DFT;
- \( - - - - \) diffuse potential

4 CONCLUSIONS

We have proposed a partially perturbative approach for formulating the Helmholtz energy functional of inhomogeneous ionic fluids. The hard sphere contribution is given by the modified fundamental measure theory, and the electrical contribution is approximated by a perturbation with respect to the corresponding bulk fluid. The quadratic term involves the second-order direct correlation function of a reference bulk fluid that is approximated by the mean-spherical approximation. The proposed density functional theory has been applied to predicting the structures and electrostatic potentials of various planar electric double layers within the restricted-primitive model. The predictions are found in good agreement with molecular simulation results. In particular, the present DFT successfully captures novel electrostatic phenomena as the counterion layering at high surface charge densities and charge inversion that can not be reproduced by alternative approaches. We found that an increase of surface charge density enhances the strength of second counterion layering. The present DFT also predicts the charge oscillations at high electrolyte concentration and shows that the excluded volume plays a crucial role in the charge inversion. In contrast, the modified Gouy-Chapmann theory (MGC) is unable to predict the charge oscillations and charge inversion phenomena because it neglects ionic size and correlations.

By considering the effect of latex surface roughness, the present DFT has also been successfully applied to calculating the \( \zeta \) potential of positively charged monodisperse polystyrene colloids in aqueous KBr solution. Good agreement between theoretical results and experimental data has been achieved. It is found that for the electrolyte concentrations studied, the values of \( \zeta \) potential for the positively charged latex-electrolyte solution interface are less than the diffuse layer potential because of surface roughness of the latex particles.

Because the modified fundamental measure theory is directly applicable to mixtures and the analytical expression for the direct correlation function of bulk mixed solutions are available in the literature, extension of the present DFT to the investigation of structures of the EDL involving counterions of different size is relatively straightforward. It is also interesting to apply the present DFT to investigating the structures and thermodynamic properties of ion-dipole mixtures at interface as the solvent (water) can be simply considered as a dipole molecule.

**NOMENCLATURE**

- \( a \) radius of latex, nm
- \( \Delta c_{ij}^{(2)}(r) \) second-order direct correlation function
- \( c \) molarity, mol·L\(^{-1}\)
- \( e \) electron charge (\( e = 1.6022 \times 10^{-19}\text{C} \))
- \( F \) Helmholtz energy functional, J
- \( k_B \) Boltzmann constant (\( k_B = 1.3806 \times 10^{-23}\text{ J·K}^{-1} \))
- \( N \) total number of ionic species
- \( n_w \) weighted density

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\[ Q \] surface charge density, C-m\(^{-2}\)
\[ r, r' \] distance between two ions, nm
\[ u(r) \] interaction potential, J-mol\(^{-1}\)
\[ w_\alpha (r) \] weight function
\[ \alpha \] index of six weight functions
\[ g(r) \] Dirac delta function
c dielectric constant
\[ \Phi \] Helmholtz energy density, J-mm\(^{-3}\)
\[ \kappa \] inverse of Debye screening length, nm\(^{-1}\)
\[ \lambda \] thermal de Broglie wavelength, nm
\[ \mu \] chemical potential, J-mol\(^{-1}\)
\[ \theta(r) \] Heaviside step function
\[ N \] number density, nm\(^{-3}\)
\[ \Omega \] grand potential, J
\[ \psi(r) \] mean electrostatic potential, J-mol\(^{-1}\)
\[ \zeta \] zeta potential, J-mol\(^{-1}\)

**Superscripts**

- b bulk
- ex excess
- ext external
- hs hard sphere
- id idea gas
- S scalar
- V vector
- \( \alpha \) index of weight function (\( \alpha = 0,1,2,3 \), V1 and V2)
- \( \mu \) reduced quantities

**Subscripts**

- C Coulomb contribution
- el electric
- hs hard sphere
- i,j ion i,j
- \( \alpha \) index of weight function (\( \alpha = 0,1,2,3 \), V1 and V2)

**REFERENCES**
