Ionic asymmetry and solvent excluded volume effects on spherical electric double layers: A density functional approach

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In this article, we present a classical density functional theory for electrical double layers of spherical macroions that extends the capabilities of conventional approaches by accounting for electrostatic ion correlations, size asymmetry, and excluded volume effects. The approach is based on a recent approximation introduced by Hansen-Goos and Roth for the hard sphere excess free energy of inhomogeneous fluids [J. Chem. Phys. **124**, 154506 (2006); J. Phys.: Condens. Matter **18**, 8413 (2006)]. It accounts for the proper and efficient description of the effects of ionic asymmetry and solvent excluded volume, especially at high ion concentrations and size asymmetry ratios including those observed in experimental studies. Additionally, we utilize a leading functional Taylor expansion approximation of the ion density profiles. In addition, we use the mean spherical approximation for multi-component charged hard sphere fluids to account for the electrostatic ion correlation effects. These approximations are implemented in our theoretical formulation into a suitable decomposition of the excess free energy which plays a key role in capturing the complex interplay between charge correlations and excluded volume effects. We perform Monte Carlo simulations in various scenarios to validate the proposed approach, obtaining a good compromise between accuracy and computational cost. We use the proposed computational approach to study the effects of ion size, ion size asymmetry, and solvent excluded volume on the ion profiles, integrated charge, mean electrostatic potential, and ionic coordination number around spherical macroions in various electrolyte mixtures. Our results show that both solvent hard sphere diameter and density play a dominant role in the distribution of ions around spherical macroions, mainly for experimental water molarity and size values where the counterion distribution is characterized by a tight binding to the macroion, similar to that predicted by the Stern model. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4876002>]

I. INTRODUCTION

The ubiquitous presence of macroions within electrolyte solutions in biological, chemical, and colloidal systems ensures that the Coulomb force is among the most important interactions to govern the behavior of these systems.^{1,2} Due to strong electrostatic interactions with the macroion surface and with each other, screening ions are not positioned randomly in three-dimensional space,^{3–6} but form a strongly correlated liquid near the surface of macroions, which leads to the formation of electric double layers (EDLs). As a result of the competition between short-range Coulomb interactions and volume exclusion interactions, due to the finite size of ions and water molecules, the correlated liquid manifests itself in a number of ways that dramatically alter the entire picture of screening. As a consequence, structural and thermodynamic properties in a small but finite volume of the liquid phase surrounding the macroion are different from those corresponding to the extended (bulk) liquid.^{7–9} These special properties of EDLs play a key role in many fundamental life processes. EDLs affect the transport of ions, water, and

a number of small molecules across cell membranes.¹⁰ Furthermore, EDLs influence structural and thermodynamic properties of the ionic atmosphere around nucleic acids, microfilaments, and various peptides associated with neurodegenerative diseases, affecting their recognition and binding affinity to other molecules and surfaces.¹¹ EDLs also play an important role in the chemical and physical properties of metal nanoparticles and their potential toxic effects on the environment and human health.¹²

One of the current limitations to understanding the molecular mechanisms underlying these phenomena is the large number of parameters that may affect the properties of EDLs. The most relevant ones are ionic size asymmetry, ionic strength, ion valence, ion hydration, solvent polarization, excluded volume effects, shape, polarization, and surface charge distribution of the macroion. These parameters have motivated widespread work in theory, experiment, and computation.^{13,14} To achieve high computational efficiency, most of the theoretical approaches for EDLs approximate the solute-liquid interface between the macroion and solvent with basic geometrical shapes such as planes, cylinders, and spheres. In particular, spherical electric double layers (SEDLs) are useful models for globular proteins,

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nanoparticle suspensions, and other colloidal systems where irregularities and inhomogeneities on the surface are expected to have a low impact on the properties of SEDLs.

Several levels of theoretical description have been proposed for describing EDLs ranging from the phenomenological Helmholtz (rigid) double layer¹⁵ to more accurate approaches based on mean-field approximations such as Gouy and Chapman diffuse^{16,17} and Stern¹⁸ models. Overall, the physics of strongly interacting charged systems is not well captured within the framework of mean-field theories including linear Debye-Huckel or nonlinear Poisson-Boltzmann (NLPB) models, since these approaches entail several approximations in their treatment of the ions and solvent molecules.¹⁹ One limitation is that the solvent is approximated by a structure-less medium of uniform dielectric constant. Additionally, properties associated with discrete ions are not considered, including correlations between ions or finite ion size, features certainly indispensable to a quantitative description of correlated screenings on macroions. For instance, within these mean field theories, like-charged objects repel in all salt conditions despite experimental observations to the contrary.^{20,21} Changing the valence of the ions in principle alters the screening contribution and thereby the strength of repulsion but does not lead to attraction.

A recent work, so-called size-modified PB theory, incorporates ion exclusion effects using a more physically meaningful lattice gas model.^{22,23} Even though size-modified PB and NLPB with Stern layer improve NLPB predictions for the diffuse part of double layers, their predictions do not match well with Molecular Dynamics (MD) results near the interface, where ion correlation and solvent crowding effects cannot be neglected.

More sophisticated theories have been proposed to address these shortcomings using functional expansions, integral equations, cluster expansions, and different flavors of density functional theory.^{24–31} These theories go beyond size-modified PB and NLPB with Stern layer since most of them include ion correlations and are quite accurate in predicting the ion distributions at the interfaces, except at high salt concentration conditions or for highly charged ions. The last decade saw a rise in the studies of EDLs based on different flavors of classical density functional theory (DFT).^{24,32,33} Within this formalism the structural and thermodynamic properties of EDLs are obtained from the definition of a generating functional, which contains contributions from coulombic forces, hard sphere steric correlations, and residual electrostatic correlations. The steric correlations arising due to the finite size of ions are modeled using either the weighted density approximation (WDA) introduced by Denton and Ashcroft,^{34,35} or the fundamental measure theory (FMT) pioneered by Rosenfeld³⁶ while the Mean Spherical Approximation (MSA) is widely used to describe the residual electrostatic correlation.^{37,38}

Almost all of the studies based on DFT for SEDLs use hard sphere models for ions and solvent.^{24,39,40} Most of them are based on a partially perturbative approach of WDA/MSA^{23,24} where the ions and solvent molecules are assumed to be of equal diameter. These studies show that for high charge densities on the macroions at low salt concen-

trations, DFT predicts a significantly greater accumulation of both counterions and co-ions near the surface when compared to the PB approach. At intermediate and high salt concentrations, the DFT predicts significant charge reversal due to ion correlation and solvent excluded volume effects.

Although results from previous models were successful in predicting the EDL properties and charge reversal, they do not account for the effects of size difference between ion species and solvent molecules, which is an important issue toward a better understanding of SEDLs in realistic systems. In this sense, an increasing number of studies for size asymmetric electrolytes have been studied recently. For instance, Guerrero-Garcia *et al.* employed the hypernetted-chain equation (HNC) coupled with MSA atomic fluid integral equation theory. In these studies, the solvent is modeled as a structureless continuous medium with a dielectric constant of 78.5 whereas ions are represented by hard spheres with different diameters. They showed that at high packing fractions, there is a charge reversal even for the low macroion surface charge.^{31,41–43} In addition, various properties of SEDLs, including the capacitance, are shown to be strongly influenced by the relative size difference between the coions and counterions. It is important to note that these results do not include solvent exclusion effects. Though the bigger ionic diameters implicitly incorporate the steric interactions arising from the volume fraction of water, they limit the macroion-ion approachability. In addition, the HNC closure approximation fails to converge for strongly asymmetric electrolytes.

In this article, we present a classical density functional theory for electrical double layers of spherical macroions that extends the capabilities of conventional approaches by accounting for electrostatic ion correlations, size asymmetry, and excluded volume effects. The approach has a number of significant advantages in comparison with the aforementioned conventional approaches. It accounts for proper and efficient description of the effects of ionic asymmetry and solvent excluded volume, specifically for high ion concentrations and size asymmetry ratios. We estimate the hard sphere excess free energy using the White Bear version of FMT II (WBFMT-II) recently introduced by Hansen-Goos *et al.*⁴⁴ It provides one of the most accurate expressions obtained for uncharged inhomogeneous multi-component hard sphere fluids, which recovers a generalization of the Carnahan-Starling-Boublik equation of state in the uniform-fluid limit. This is relevant for the proper and efficient description of water excluded volume and asymmetric ion size effects on SEDLs at experimental sizes and concentrations.^{30,44–46} It improves upon those conventional models where a diameter of 4.25 Å is often considered for all ion species and solvent molecules (if solvent is included explicitly). While this value for the diameters is a good approximation to model the aqueous diameters of cations, the anions are bigger and the water molecules are smaller. This simplification hence, leads to either over- or under-estimation of steric interactions. The usage of a single diameter for all the particles has also a high impact in the description of adsorption characteristics at charged surfaces since it yields the same counterion-macroion, coion-macroion and water-macroion contact distance values. Accordingly, the use of the WBFMT-II approximation in our theoretical

formulation provides a more accurate description of the underlying physics at solute-liquid interfaces. Additionally, the electrostatic ion correlation effects are taken into account by utilizing a leading functional Taylor expansion approximation in power of the ion density profiles and the MSA for multi-component charged hard sphere fluids. These approximations are implemented in our theoretical formulation into a suitable decomposition of excess free energy, which plays a key role in capturing the complex interplay between charge correlations and excluded volume effects. This novel coupling between the WBFMT-II approximation for the hard sphere correlation and the MSA for the residual electrostatic correlation incorporates important structural features of spherical EDLs without increasing significantly the computational cost. When compared with full atomistic simulations, our computational model becomes an extremely useful tool for studying thermodynamic and structural properties of spherical EDLs, where a good balance between accuracy and efficiency in predicting ion density profiles is highly desired. This is of significant relevance mainly for those properties requiring repeated calculations of the ion density profiles, and under multiple environments and solute morphology.

We apply the proposed computational approach to describe the role that the ion size, ion size asymmetry, and solvent excluded volume play on the ion profiles, integrated charge, mean electrostatic potential, and ionic coordination number around spherical macroions at various electrolyte mixture conditions. We perform Monte Carlo simulations to validate the proposed approach in various scenarios obtaining a good compromise between accuracy and computational cost. Then, we analyze symmetric and asymmetric electrolytes using different ion and solvent models. We describe the role that these properties play on the divalent versus monovalent ion competition and the ion preferential selectivity by the spherical macroion.

II. THEORETICAL FORMULATION

A. Model

The system considered in this approach consists of a rigid charged spherical solute surrounded by an electrolyte solution comprised of m ionic species. Each ion of species i is represented by bulk density ρ_i^0 , a charged hard sphere of diameter σ_i , and total charge ez_i , where e is the electron charge and z_i is the corresponding ionic valence. We use the point-like charge model in such a way that the total charge of the ions is embedded at their centers. This model allows us to describe the electrostatic interaction between ions in a continuum dielectric medium of dielectric constant ϵ using the Coulomb's law and the total ion-ion pair-potential in the following expression:

$$u_{ij}(r) = \begin{cases} \infty, & r < R_{ij} \\ \frac{z_i z_j e^2}{\epsilon r}, & r > R_{ij}, \end{cases} \quad (1)$$

where $i, j = 1, \dots, m$, $R_{ij} = (\sigma_i + \sigma_j)/2$, and r is the ion-ion separation distance.

Additionally, we use several representative models for the ions and solvent to elucidate the role of the solvent ex-

FIG. 1. Schematic representation of the different models employed in this work: (a) restricted primitive model (RPM), (b) primitive model (PM), (c) solvent restricted primitive model (SRPM), and (d) solvent primitive model (SPM). In the SRPM and SPM models, the size of small solvent hard spheres is 2.75 Å at a molar concentration 55.56 M. The hydrated ion sizes used for the RPM and PM models are bigger than the bare ion sizes used for the SRPM and SPM models. In the PM and SPM models, ion sizes are allowed to be different for different species, whereas in the RPM and SRPM models, ion sizes are restricted to a single value for all species.

cluded volume and ionic size asymmetry effects on the ion density profiles around spherical macroions. We consider two solvent models, namely, the primitive model (PM) and the solvent primitive model (SPM). In the simpler primitive model, the solvent molecule size and solvent correlation effects are neglected. Meanwhile, the solvent electrostatics is modeled as a continuum dielectric environment with a dielectric constant $\epsilon = 78.5$. In the hybrid solvent primitive model approach, the electrostatics of the solvent is considered implicitly by using the continuum dielectric model described above, but the steric interaction is incorporated explicitly by considering the solvent molecules as a neutral hard sphere. When the hard sphere sizes of all species are equal, the resulting primitive and solvent primitive models are termed restricted primitive model (RPM) and solvent restricted primitive model (SRPM), respectively. A pictorial representation of the four models is given in Fig. 1.

In regards to the description for the spherical macroion, a hard sphere of radius R and uniform surface charge density $\sigma = Ze/4\pi R^2$ is used to represent the solute, where Z represents the solute valence. Additionally, the presence of the solute in the bulk electrolyte is modeled as an external potential $v_i(r)$ acting on each ion species i . The resulting inhomogeneous ion density profiles $\rho_i(r)$ are calculated from pair correlation functions and functional expansions around the bulk ionic densities $\rho_1^0, \rho_2^0, \dots, \rho_m^0 (\equiv \{\rho_j^0\})$ using density functional theory. Under this framework, the interplay between charge correlations and excluded volume effects is better described by treating the steric and electrostatic contributions to the ion density profiles in different ways. The hard sphere contributions are estimated through weighted density function approximations. The residual electrical contributions are calculated perturbatively around the uniform fluid. A detailed description of the theoretical approach is given below.

B. Density functional theory for inhomogeneous fluid mixtures

The density functional theory for inhomogeneous fluid mixtures is based on the definition of a generating functional from which the structural and thermodynamic properties of the system can be obtained. The details of this approach are discussed elsewhere.^{47,48} However, for the completeness of this article, we summarize them below. The generating functional of the density profiles is given by the grand potential $\Omega[\{\rho_j\}]$ which is the Legendre transform of the Helmholtz free energy of the system $F[\{\rho_j\}]$

$$\Omega[\{\rho_j\}] = F[\{\rho_j\}] + \sum_{i=1}^m \int dr \rho_i(r) \{v_i(r) - \mu_i\}, \quad (2)$$

where μ_i represents the chemical potential of the i th ionic component. The Helmholtz free energy functional is generally expressed as the sum of the ideal gas F^{id} and the excess F^{ex} free energies. The former is known exactly, but approximations must be developed for the latter. At equilibrium, the grand potential functional is minimal with respect to variations in the density profiles, yielding the following formally exact expression for the singlet ion density profiles $\{\rho_i(r)\}$:

$$\rho_i(r) = \rho_i^0 \exp\{\Delta c_i^{(1)}(r; \{\rho_j\}) - \beta q_i \psi^{Solute}(r) - \beta v_i^{hs}(r)\}, \quad (3)$$

where we have used the definitions $\Delta c_i^{(1)}(r; \{\rho_j\}) \equiv c_i^{(1)}(r; \{\rho_j\}) - \tilde{c}_i^{(1)}(\{\rho_j^0\})$, $v_i(r) \equiv q_i \psi^{Solute}(r) + v_i^{hs}(r)$, the one particle direct correlation function for inhomogeneous fluids $c_i^{(1)}(r; \{\rho_j\})$

$$c_i^{(1)}(r; \{\rho_j\}) = -\beta \frac{\delta F^{ex}[\{\rho_j\}]}{\delta \rho_i(r)}, \quad (4)$$

and $\tilde{c}_i^{(1)}(\{\rho_j^0\})$ is the corresponding correlation for uniform fluids. In these definitions $v_i^{hs}(r)$ represents the excluded volume potential energy generated by the spherical hard macroion on an ion of species i located at a distance r from the center of the macroion, e.g.,

$$v_i^{hs}(r) = \begin{cases} 0, & r > R + \sigma_i/2 \\ \infty, & \text{otherwise.} \end{cases} \quad (5)$$

On the other hand, $\psi^{Solute}(r)$ represents the mean electrostatic potential generated by the macroion surface charge, and consequently $q_i \psi^{Solute}(r)$ accounts for the electric potential energy required by the fixed macroion surface charge to bring an ion of species i from infinity to a distance r from the center of the macroion.

Substituting Eq. (5) into Eq. (3), we obtain the following expression for the ion density profiles:

$$\rho_i(r) = \begin{cases} \rho_i^0 \exp\{\Delta c_i^{(1)}(r; \{\rho_j\}) - \beta q_i \psi^{Solute}(r)\}, & r > R + \sigma_i/2 \\ 0, & r \leq R + \sigma_i/2. \end{cases} \quad (6)$$

Clearly, the explicit expression for the ion density profiles (6) depends on the way the excess Helmholtz free energy

of the system $F^{ex}[\{\rho_j\}]$ is approximated. A convenient expression for the ion profiles is obtained when the excess free energy F^{ex} is calculated as follows:

$$F^{ex}[\{\rho_j\}] = F_{Coul}^{ex}[\{\rho_j\}] + F_{hs}^{ex}[\{\rho_j\}] + F_{res}^{ex}[\{\rho_j\}], \quad (7)$$

where the first term

$$F_{Coul}^{ex}[\{\rho_j\}] = \frac{1}{2} \sum_i \sum_k q_i q_k \int \int d\mathbf{r} d\mathbf{r}' \frac{\rho_i(r) \rho_k(r')}{|\mathbf{r} - \mathbf{r}'|} \quad (8)$$

represents the pure Coulomb contribution generated by the ionic distributions in the van der Waals type approximation, whereas the second and third terms, $F_{hs}^{ex}[\{\rho_j\}]$ and $F_{res}^{ex}[\{\rho_j\}]$, represent the pure hard sphere and remaining (“residual” correlation) contributions, respectively. Notice that setting $F_{hs}^{ex}[\{\rho_j\}] = F_{res}^{ex}[\{\rho_j\}] = 0$ yields the following first functional derivative of the excess free energy:

$$\begin{aligned} c_i^{(1)}(r; \{\rho_j\}) &= -\beta \frac{\delta F^{ex}[\{\rho_j\}]}{\delta \rho_i(r)} = -\beta q_i \sum_k q_k \int d\mathbf{r}' \frac{\rho_k(r')}{|\mathbf{r} - \mathbf{r}'|} \\ &= -\beta q_i \psi^{ion}(r, \{\rho_j\}), \end{aligned}$$

where $\psi^{ion}(r, \{\rho_j\})$ represents the mean electrostatic potential due to the ionic distributions. By substituting the above expression into Eq. (6), we recover the conventional non-linear Boltzmann distribution approximation for the ion species i ,

$$\rho_i(r) = \begin{cases} \rho_i^0 \exp\{-\beta q_i \psi(r, \{\rho_j\})\}, & r > R + \sigma_i/2 \\ 0, & r \leq R + \sigma_i/2, \end{cases} \quad (9)$$

where $\psi(r, \{\rho_j\}) \equiv \psi^{Solute}(r, \{\rho_j\}) + \psi^{ion}(r, \{\rho_j\})$ represents the mean electrostatic potential due to the macroion surface charge plus the ion distributions.

Accordingly, the additional terms $F_{hs}^{ex}[\{\rho_j\}]$ and $F_{res}^{ex}[\{\rho_j\}]$ appearing in Eq. (7) provide corrections to the continuum NLPB predictions, and may be responsible for capturing charge inversion, charge-dependent asymmetry, and other important phenomena characterizing highly charged interacting systems.^{40,49} More importantly, the decomposition (7) is able to switch “on” ($F_{res}^{ex}[\{\rho_j\}] \neq 0$ and/or ($F_{hs}^{ex}[\{\rho_j\}] \neq 0$) and “off” ($F_{res}^{ex}[\{\rho_j\}] = 0$ and/or ($F_{hs}^{ex}[\{\rho_j\}] = 0$) charge correlations ($F_{res}^{ex}[\{\rho_j\}]$) and excluded volume ($F_{hs}^{ex}[\{\rho_j\}]$) effects upon the Poisson Boltzmann predictions ($F_{Coul}^{ex}[\{\rho_j\}]$), something that is extremely useful for understanding molecular mechanisms and identifying relevant parameters that may dominate their structural and thermodynamic properties of SEDLs at specific ionic conditions and solute morphology.

The final expressions for the ion density profiles are obtained by substituting Eq. (7) into Eq. (4) and the resulting

expression into Eq. (6):

$$\rho_i(r) = \begin{cases} \rho_i^0 \exp\{-\beta q_i \psi(r, \{\rho_j\}) + \Delta c_i^{(1)hs}(r; \{\rho_j\}) + \Delta c_i^{(1)res}(r; \{\rho_j\})\}, & r > R + \sigma_i/2 \\ 0, & r \leq R + \sigma_i/2, \end{cases} \quad (10)$$

where $c_i^{(1)hs}(r; \{\rho_j\})$ and $c_i^{(1)res}(r; \{\rho_j\})$ are the hard sphere and residual electrostatic one particle direct correlation functions, respectively.

Notice that the expressions obtained for the ion distributions (10) provide detailed description of structural as well as thermodynamic properties of EDLs. For instance, the coordination number $N_\alpha(r)$ gives the average ion number of species i that will be found in a sphere of radius r centered on the nanosphere. It is calculated in terms of the ion density profiles by the following expression:

$$N_j(r) = 4\pi \int_R^r \rho_j(r') r'^2 dr'. \quad (11)$$

On the other hand, the integrated charge distribution $P(r)$ surrounding the macromolecule is given by

$$P(r) = Z + \int d\mathbf{r}' \sum_i z_i \rho_i(\mathbf{r}'). \quad (12)$$

The mean electrostatic potential $\psi(r, \{\rho_j\})$ due to the macroion surface and the ion distributions in a solvent with isotropic and constant relative permittivity ϵ can be calculated from the integrated charge distribution $P(r)$ and the use of Gauss's law. Alternatively, it can be obtained by solving the Poisson equation

$$\nabla^2 \psi(r, \{\rho_j\}) = -\frac{1}{\epsilon} \sum_{i=1}^m \rho_i(r) z_i, \quad (13)$$

and using the boundary conditions $\psi(r, \{\rho_j\})|_{r \rightarrow \infty} \rightarrow 0$, $\epsilon \partial \psi(r, \{\rho_j\}) / \partial r|_{r=R} = -\sigma = -Ze/4\pi R^2$ and the electroneutrality condition:

$$\int_R^\infty \sum_{i=1}^m z_i \rho_i(r) d\mathbf{r} + Z = 0.$$

The solution of Eq. (13) in spherical coordinates reads

$$\psi(r, \{\rho_j\}) = \frac{4\pi e}{\epsilon} \int_r^\infty \sum_i z_i \rho_i(r') \left(r' - \frac{r'^2}{r} \right) dr' \quad r > R. \quad (14)$$

Detailed description of the approximations used in hard sphere and residual electrostatic correlation functions and the computational details of the theoretical calculations and the Monte Carlo simulations are given in the Appendix.

III. DISCUSSION AND RESULTS

A. Comparison between predictions and simulation results

We compare the results predicted by several theoretical approaches with MC simulation in various scenarios for testing purposes. One of these approaches is our proposal (WBFMT-II + MSA), namely, the WBFMT-II approximation for the hard sphere correlation coupled with the MSA

FIG. 2. Macroion-ion radial distribution functions (RDF's) predicted by different theoretical models for 1:1 RPM electrolyte at 1 M concentration. x-axis represents distance from the macroion surface. Symbols denote the GCMC simulation results, and lines correspond to theoretical predictions. Filled symbols describe the counterion profile, empty symbols correspond to the coion profile. Solid curves correspond to WDA predictions, dashed lines represent the modified FMT predictions.

for the residual electrostatic correlation. The second approach (WDA + MSA) is based on the WDA for the hard sphere correlation coupled with MSA for the residual electrostatic correlation.^{26,40}

For 1:1 RPM electrolyte with equal sized ions at 1 M (Molar) concentration, we do not observe significant deviation between the ion density profiles predicted by these theories and MC simulation results (see Fig. 2). At the macroion-ion contact point, the counterion density predicted by WDA + MSA is nominally better than that of WBFMT-II + MSA. With the inclusion of solvent interactions, WBFMT-II + MSA results are closer to the corresponding MC simulation data when compared to WDA + MSA as shown in Fig. 3. However, the difference between the WDA + MSA

FIG. 3. RDF plots of 1 M, 1:1 SRPM electrolyte. The top and the bottom *rdfs* correspond to counter ions and coions, respectively, whereas the middle curve represent macroion-solvent *rdf*. Symbols are GCMC simulation results. Upward triangles describe the counterion profile, downward triangles correspond to the coion profile, and filled triangles show the solvent profile. The MC data are taken from Patra's paper.⁴⁰

FIG. 4. Macroion-ion *rdf*'s of 0.5 M 2:2 primitive model electrolyte surrounding a macroion with radius of 5 Å and a surface charge density of 0.407 C/m². The diameters of coions and counterions are (a) 8.5 Å and 4.25 Å, and (b) 4.25 Å and 8.5 Å, respectively. Solid lines are WBFMT-II predictions, dashed lines are WDA predictions, and symbols are GCMC simulation data.

and WBFMT-II + MSA results for the two size symmetric models is minor, and we can consider the predictions of both the theories accurate.

For an electrolyte with ionic size asymmetry, when the counterions are smaller than coions, we observe that WDA prediction deviates significantly from MC results (see Fig. 4). When the counterions are bigger than coions, the difference between WDA + MSA prediction and MC data is reduced. Nonetheless, the difference is still significant whereas WBFMT-II + MSA predictions for both cases are in good agreement with simulation data.

B. Structural and thermodynamic properties of spherical double layers

1. Solvent excluded volume effects

Recent reports indicate that explicit inclusion of water molecules in Monte Carlo and molecular dynamics simulations gives a better prediction of the properties of EDLs.^{40,50,51} Incorporating neutral solvent molecules in SEDL simulations is shown to give rise to layering and to affect the charge inversion. However, the influence of hard sphere size and the difference in solvent and ion sizes on the properties of SEDL has not been explored. A single value of 4.25 Å is typically used for ion and solvent (water) diameters.⁴⁰ This value is very high when compared to the experimental diameter of water (2.75 Å). Also, it is not clear what happens when the size of the solvent is different from the size of ions. For example, typical aqueous ionic diameters for anions are smaller than 4.25 Å but bigger than the diameter of water molecule. Also, cation diameters are even smaller⁵² than the diameter of water molecule.

We first employ a solvent restricted primitive model to study how the hard sphere size affects the properties of SEDLs. For the solvent primitive model, where solvent is explicitly included, the partial packing fraction of the solvent,

given by $\eta_i = \pi/6\rho_i\sigma_i^3$, is fixed at 0.363. This value is obtained from the known molarity of water (55.5 M) and its molecular diameter (2.75 Å).⁵³ This value is slightly different from the experimental value of the packing fraction of water, 0.343,⁵⁴ due to the hard sphere approximation for the water molecule. This results in different molar densities of solvent molecules for different hard sphere diameters. The total packing of the electrolyte, η , is given by the sum of the partial packing fractions of ions and the solvent molecules.

Fig. 5 shows the normalized density profiles or radial distribution functions (*rdf*) of the SRPM electrolyte with different hard sphere diameters: 2 Å, 3.5 Å, and 5.0 Å. For comparison, the normalized density profiles of the RPM electrolyte with corresponding HS diameters are shown in Fig. 6.

When the solvent excluded volume effects are omitted, the counterion density profile has an exponential monotonic decay to the ionic bulk density. This is similar to the exponential decay behavior obtained by approaches based on Debye-Huckel theory. The probability of finding coions also increases monotonically with the separation distance from the nanoparticle surface. This is a consequence of the high repulsive electrostatic interaction acting on the coions at short separation distances due to the nanoparticle surface charge.

On the other hand, a transition to oscillatory behavior occurs when the solvent excluded volume is incorporated. The first layer of the counterion *rdf* has a very sharp peak at the contact point, indicating that the first shell of counterions are tightly bound to the macroion. The counterions in the first shell are called *indifferent adsorbing* ions.⁵⁵ The magnitude of the this first peak increases with HS diameter for all species. Fig. 5 also shows that the oscillation period in the ion and solvent *rdf*'s is equal to the hard sphere diameter. The magnitude of the second peak, however, decreases with increasing the HS diameter for counter ions. For coions, the trend is in the opposite direction.

The resulting mean electrostatic potential (MEP) and the integrated charge distribution are plotted in Fig. 7 for SRPM

FIG. 5. Normalized ion density profiles in an SRPM 1 M 1:1 electrolyte surrounding a macromolecule of 1.5 nm radius and 0.102 C/m² surface charge. The HS diameters are 2.0 Å (red solid line), 3.5 Å (green dashed line), and 5.0 Å (blue dashed-dotted line).

and RPM electrolytes. The magnitude of the MEP of an SRPM electrolyte at the surface of macroion is smaller than that of the corresponding the RPM electrolyte. Within the Helmholtz region (where the potential is linear), the magnitude of the slope of MEP of SRPM electrolyte is steeper. Also within the Helmholtz region, the variation in MEP with respect to HS diameter is smaller in SRPM electrolyte. At the surface of macroion, the change in MEP of RPM electrolyte is 3 times larger than that of SRPM electrolyte. For 5 Å HS diameter, charge inversion is predicted for both SRPM and RPM electrolytes.

In the diffuse region of the SEDL, the MEP of SRPM electrolyte shows a greater variation when compared to that of RPM electrolyte. This means that for SRPM electrolytes, HS diameter has a greater impact on zeta potential, which is

the potential value at the slippage plane in the diffuse part of the SEDL and determines the stability of colloidal systems. Though ambiguous, the location of the slippage plane is close to the Helmholtz plane.

The integrated charge distribution plots of the SRPM electrolytes are markedly different to those of RPM electrolytes. For SRPM electrolyte, the integrated charge distribution drops off rapidly due to the large magnitude of counterion density at the contact. The magnitude of the drop in the integrated charge is larger when the HS diameter is bigger. This means that in SRPM electrolyte, a bigger HS diameter leads to more effective screening of the surface charge. Also, the layers in the SRPM ion densities lead to shoulder formation in the charge distribution plots. In the RPM electrolyte, the charge drop is smooth and gradual, and no shoulders are present.

To isolate the role of the solvent HS diameter, we vary the HS diameter of solvent molecules while keeping the HS diameters of ions and the total packing fraction fixed. Plots (a) and (b) in Fig. 8 show the resulting ion density profiles. The magnitude of the first peak at the contact point for both counterions and coions is larger when the size of the solvent molecule is smaller. The oscillation period in the ion density profiles is equal to the solvent hard sphere diameter. For smaller solvent HS diameter, 2 Å, the magnitude of the secondary peak in counterion profile is bigger when compared with the bigger ion size cases. The bigger secondary peaks lead to a pronounced shoulder for the 2 Å solvent HS diameter in the integrated charge density plot shown in Fig. 9(a). Surprisingly the integrated charge density plot for 5 Å solvent HS diameter, has no shoulder due to the near absence of layering in ion density profile. These plots show that the solvent molecule size has to be less or close to the size of ions to observe the layering effect.

The MEP plot in Fig. 9(a) shows that within the Helmholtz region of the SEDL, there is no variation in the potential due to variation in solvent HS size. However, the potential in the diffuse region of the SEDL shows variation due to change in the solvent HS size. When the ion sizes are increased to 5 Å, the variation in the potential within the

FIG. 6. Normalized ion density profiles in an RPM electrolyte with the concentration and macromolecule parameters equal to those in Fig. 5. The key is same as that in Fig. 5.

FIG. 7. Reduced mean electrostatic potential, $\beta\psi$, and charge distribution, P , in a 1 M 1:1 electrolyte of types (a) SRPM and (b) RPM surrounding a macromolecule of 1.5 nm radius and 0.102 C/m² surface charge. The HS diameters are 2.0 Å (red solid line), 3.5 Å (green dashed line), and 5.0 Å (blue dashed-dotted line).

diffuse region of the SEDL due to variation in solvent molecule size is more pronounced as shown in Fig. 9(b).

To understand the role of ion size on the properties of SEDLs, the ion HS diameters are varied while keeping the

solvent HS size fixed. The resulting MEP plot in Fig. 10(a) shows that varying the ion HS diameter produces greater variation in the potential within the diffuse region. The potential in the Helmholtz region also varies with respect to the ion HS

FIG. 8. Normalized density profiles of (a) counterions, (b) co-ions, and (c) solvent molecules in a 1 M 1:1 electrolyte surrounding a macromolecule of 1.5 nm radius and 0.102 C/m² surface charge with ion HS diameters fixed at 3.5 Å. The solvent HS diameters are 2.0 Å (red solid line), 3.5 Å (green dashed line), and 5.0 Å (blue dashed-dotted line).

FIG. 9. Reduced mean electrostatic potential, $\beta\psi$, and charge distribution, P , in a 1 M 1:1 SPM electrolyte surrounding a macromolecule of 1.5 nm radius and 0.102 C/m^2 surface charge with ion HS diameters fixed at (a) 3.5 Å and (b) 5 Å. The solvent HS diameters are 2.0 Å (red solid line), 3.5 Å (green dashed line), and 5.0 Å (blue dashed-dotted line).

size, but the variation is less when compared to that of diffuse region. However, due to the fact that solvent HS variation does not produce any change in MEP in the Helmholtz region, the potential variation within the Helmholtz region observed for SRPM electrolytes is due to the size of the ions only. When the ion HS diameter is 5 Å, charge inversion is observed, even when the solvent HS diameter is 3.5 Å. This indicates that again HS size of ions and not that of solvent molecules is responsible for charge inversion.

The MEP plot of the above electrolyte at a reduced concentration of 0.1 M ionic strength in Fig. 10(b) shows that at lower ionic strengths, ion size variation has negligible effect on the diffused SEDL. However due to the high partial packing fraction of the solvent molecules, the counterions are adsorbed to the surface of the macroions as indicated by the drop in the charge at the contact point.

2. Ionic size asymmetry effects

A number of studies on ionic size asymmetry effects on the SEDL within the context of the primitive model have been reported in literature.^{31,41,42} But ionic size asymmetry effects

within the solvent primitive model for spherical double layers have not been explored so far. Ionic diameters corresponding to aqueous and crystalline states and first hydration shell for few ions are listed in Table II. These diameter values are smaller than 4.25 Å. Rakitin and Pack⁵⁰ in their analysis of ion distribution surrounding micelles show that ion radii without hydration shell are a better measure of ion size when solvent is explicitly incorporated. Hence, for asymmetric ions in solvent primitive model, we use Marcus⁵² ionic diameters. For primitive model, we employ first hydration shell diameters of the ions. This results in partial inclusion of solvent volume effects in the primitive model.

To isolate the effect of ionic size asymmetry, we use RPM2 and SPM2 models listed in Table I, where the diameters of equal sized cations and anions are adjusted such that the resulting ionic partial fraction is equal to the ionic partial fraction in asymmetric ion electrolytes. To that effect, the ion HS diameters in the RPM2 are increased to 5.59 Å so that partial fraction due to ions becomes 0.11 again. 3.04 Å is used for the ion diameter in the SPM2 electrolyte. Fig. 11 shows the ion density profiles of 1 M NaCl predicted by three different ion size models for primitive and solvent primitive

FIG. 10. Reduced mean electrostatic potential and charge distribution in 1:1 SPM electrolytes of strengths (a) 1 M and (b) 0.1 M surrounding a macromolecule of 1.5 nm radius and 0.102 C/m^2 surface charge with solvent HS diameter fixed at $3.5 \text{ \AA}$. The ion HS diameters are $2.0 \text{ \AA}$ (red solid line), $3.5 \text{ \AA}$ (green dashed line), and $5.0 \text{ \AA}$ (blue dashed-dotted line).

models. The RPM1 and SRPM1 models are also considered due to the wide spread use of $4.25 \text{ \AA}$ as HS diameter.

Fig. 11(b) shows the difference between ion *rdf*'s within the primitive model. Due to the different ion sizes, the macroion contact distances for the ion *rdf*'s are different. The magnitudes of counterion densities at the contact point are slightly different. There is a 16.9% increase in counterion density at contact point for the primitive model when compared to $4.25 \text{ \AA}$ ion size restricted primitive model. The ions density profiles predicted by the three primitive models are monotonic. The resulting MEP and integration charge density plots are shown in Fig. 12(b). Though the PM and RPM2 have equal packing fractions, using primitive model with asymmetric ion sizes results in higher MEP and integrated charge with

in the double layer region. Charge amplification is observed in the case of primitive model near the contact point.

The ion profiles predicted by the three solvent primitive models are shown in Fig. 11(a). The width of the first peak in the counterion density is proportional to the counterion HS diameter. The size asymmetric solvent primitive model, SPM1, predicts higher counterion density and lower coion density at the contact when compared with the SPM2 model, which has the same packing fraction as that of the SPM1. All the three solvent primitive models predict counter ion density greater than the bulk density at the contact point. This indicates that solvent excluded volume induced surface affinity overcomes the strong coulombic repulsive forces experienced by the coions near the surface of the macroion. However, in the SPM1 model, due to the smaller size of coions relative to the counterions, the repulsive potential experienced by coions is greater when compared to SPM1 and

TABLE I. Electrolyte models.

#	Model	Ionic HS diameter	Solvent diameter	Solvent concentration	η
1	RPM1	$4.25 \text{ \AA}$	...	...	0.048
2	PM	Hydration dia. in Table II	...	...	0.110
3	RPM2	$5.59 \text{ \AA}$	...	...	0.110
4	SRPM1	$4.25 \text{ \AA}$	$4.25 \text{ \AA}$	15M	0.411
5	SPM1	Aqueous dia. in Table II	$2.75 \text{ \AA}$	55.5M	0.381
6	SPM2	$3.04 \text{ \AA}$	$2.75 \text{ \AA}$	55.5 M	0.381

TABLE II. Hard sphere ionic diameters in Angstroms.

#	Element	Aqueous ⁵²	Crystalline ⁷⁰	First hydration shell ⁵²
1	Na^+	1.96	2.32	4.74
2	K^+	2.68	3.04	5.46
3	Mg^{2+}	1.44	1.72	4.22
4	Cl^-	3.66	3.34	6.24
5	Br^-	3.88	3.64	6.66

FIG. 11. Normalized ion density profiles in 1 M and 1:1, (a) SPM and (b) PM electrolytes surrounding a macromolecule of 1.5 nm radius and 0.102 C/m² surface charge. The solvent primitive models are SPM with aqueous ionic diameters given in Table II (red solid lines), SPM with ion HS diameter of 3.04 Å (green dashed lines), and SPM with ion HS diameter of 4.25 Å (blue dashed-dotted lines). In all the models solvent has HS diameter of 2.75 Å and a molar density of 55.5 M. The primitive models are PM with hydration shell diameters given in Table II (red solid lines), RPM with HS diameter of 5.59 Å (green dashed lines), and RPM with HS diameter of 4.25 Å (blue dashed-dotted lines). Lines represent DFT results and symbols represent GCMC results.

FIG. 12. Reduced mean electrostatic potential and charge distribution for electrolytes described in Fig. 11. The key is same as that of Fig. 11.

FIG. 13. Number of counterions and coions surrounding the macromolecule for electrolytes described in Fig. 11. The key is same as that of Fig. 11.

SRPM1 models. The MEP plot for the three SPM models given in Fig. 12(a) shows that the SPM1 and SPM2 models predict almost equal potential in the diffuse region. In the Helmholtz region, the SRPM1 and SPM2 have practically identical potential values. This is due to the counterion HS sizes in the SPM1 and SPM2 models being close. The potential of the SPM1 model is slightly higher in the Helmholtz region due to the charge amplification caused by excess coions in the macromolecule vicinity.

The ion count values for these different models are shown in Fig. 13. In the primitive model, the ion count for both coions and counterions increases gradually whereas in the solvent primitive model, only the coion count increases gradually, and the counterion count rises to a high value within a short distance from the macroion-ion contact point. This shows that the solvent primitive model favors tight binding of counterions to the macroion (indifferent adsorption) when compared to the primitive model.

3. 2:1 electrolyte

In Secs. III B 1–III B 2 we have analyzed the ion and solvent hard sphere size effects. Mean electrostatic potential and integrated charge profiles $P(r)$ shed also useful light on the effects of mono and divalent ions on the electrostatic properties of spherical double layers. The MEP and $P(r)$ plots for 1:1 and 2:1 electrolytes are shown in Fig. 14. Here for a direct comparison, the ion diameters used with solvent primitive model are identical to those used with primitive model. We note that

in all the electrolytes analyzed, the PM generates very weak charge inversion. Also, charge inversion is very weak in NaCl electrolytes for both models (see Fig. 14(a)). Indeed, the solvent excluded volume affects the behavior of the integrated charge reducing the MEP when compared with that generated by PM. There is a significant charge amplification close to the nanoparticle surface due to the accumulation of coions followed by a rapid decrease of the integrated charge. This causes a vertical down shift of the MEP at distance close to the nanoparticle surface. However, this shift is not large enough to make the MEP cross the zero-line at larger distances. The solvent volume exclusion also modifies the monotonic decrease of the integrated charge by introducing an asymptotic wavelike behavior.

A different scenario is observed for divalent electrolytes as shown in Fig. 14(b). In MgCl_2 salts at 0.5 M concentration, enhanced electrostatic correlation is generating charge inversion. This shows that the higher the ion valence charge is, the more pronounced is the charged inversion.

Finally, the MEP of electrolyte mixtures, where 2:1 electrolyte at different strengths is added to 1 M fixed strength 1:1 electrolyte are shown in Fig. 15. We mix NaCl/ MgCl_2 electrolyte salts at $[\text{Mg}]:[\text{Na}]$ concentration ratios of 0, 0.125, 0.25, and 0.5. The resultant 1:2:1 electrolyte mixture is modeled with both primitive and solvent primitive models using ionic hydration shell diameters for the size of the ions. The MEP plots shown in Fig. 15 reveal richer charge inversion, where complex interactions arising from ion size asymmetry, ion valence asymmetry, ion bulk density differences,

FIG. 14. Mean electrostatic potential and integrated charge for (a) 1 M 1:1 electrolyte and (b) 0.5 M 2:1 electrolyte. Red solid lines represent PM, green dashed lines correspond to SPM.

FIG. 15. Mean electrostatic potential of 1:2:1 electrolytes as a function of radial distance from the surface of the macroion. The strength of 1:1 electrolyte is 1 M and the relative strength of 2:1 electrolyte with respect to 1:1 electrolyte is (a) 0, (b) 0.125, (c) 0.25, and (d) 0.5. Red solid lines represent PM, green dashed lines correspond to SPM.

and solvent volume exclusion contribute to the electrostatic properties of SEDLs.

IV. CONCLUSIONS

In this article we introduce a hard sphere model based classical density functional theory for EDLs of spherical macroions that accounts for electrostatic ion correlations, size asymmetry, and excluded volume effects. Using the solvent primitive model and by varying the diameters for each species, we address the role that ion size, ion correlation, and solvent excluded volume play on the ion profiles, integrated charge, mean electrostatic potential, and ionic coordination number at different ionic conditions. We find that the solvent hard sphere diameter has a significant impact on the layering of ions predicted by solvent primitive models. This layering directly influences the integrated charge and mean electrostatic potential in the diffuse region of the SEDL. We expect the choice of solvent HS diameter to have noticeable impact on the calculation of zeta potential. Hence, solvent partial packing fraction alone is not enough to properly account for the solvent steric interactions. Both concentration and solvent hard sphere diameter have to be taken into consideration. We also find that the counterion count increases gradually in the primitive model whereas in the solvent primitive model, the counterion count rises to high value within a short distance from the macroion-ion contact point. This shows that the solvent primitive model favors tight binding of counterions to the macroion (indifferent adsorption) when compared to the primitive model.

Based on the results presented in this paper, we conclude that the modeling of solvent molecules with known concentration and size values is essential in the characterization of spherical double layers. Both of them are shown to play a fundamental role in the competition between the ionic charge correlations and the excluded volume effects of solvent molecules that govern the SEDL properties. Additionally, by modeling ions with hard spheres of different diameters, it is found that the ion density profiles exhibit complex layering behavior depending the size ratios of coions, counterions, and the solvent molecules.

Overall, modeling SEDLs with WBFMT-II + MSA offers important advantages. It accounts for the proper and efficient description of the effects of ionic asymmetry and solvent excluded volume. This is of significant importance in modeling more realistic electrolytes containing water at experimental size and concentration, and ions of different sizes. Additionally, it accounts for electrostatic ion correlation effects at low computational cost. When compared with full atomistic simulations, our computational model becomes an extremely useful tool for studying thermodynamic and structural properties of spherical EDLs where a good balance between accuracy and efficiency in predicting ion density profiles is highly desired. This is of significant relevance mainly for those EDL properties requiring repeated calculations of the ion density profiles and under multiple environments and solute morphology. For instance, the WBFMT-II + MSA may be useful for calculating (solvation) free energy, potential of mean force, and entropy using either the thermodynamic integration or the

coupling parameter methods where full atomistic simulations may be inappropriate due to the extremely high computational demand for the modeling of explicit water molecules and long range interactions.⁵⁶

In addition, the proposed DFT is potentially useful for studying highly charged interacting systems where ion-ion correlations and solvent excluded volume may be responsible for capturing physical effects that go beyond mean field approximations. For example, the proposed DFT can be used to study the osmotic pressure generated by high ionic strength mixtures of aqueous electrolytes in certain biological conditions, which plays an important role in the emerging field of nanoparticle drug delivery.^{3,57}

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APPENDIX: CORRELATION FUNCTIONS AND COMPUTATIONAL METHODS

1. Hard sphere direct correlation function approximation: Fundamental measure theory

Several approaches have been reported in the literature to calculate the hard sphere ion correlation functions $c_i^{(1)hs}(r, \{\rho_j\})$ appearing in Eq. (10). One popular approach is the weighted density approach pioneered by Denton and Ashcroft.^{34,35} Patra and his colleagues successfully applied WDA for EDLs of RPM and SRPM electrolytes at different geometrical interfaces.^{24,25,39,58,59} However, the single weighted density used in WDA is not sufficient enough to account for the steric interactions in primitive and solvent primitive electrolytes containing ionic size asymmetry. Thus, we base our study on modified fundamental-measure theory,^{36,47} a generalized form of WDA. FMT accounts for the different sizes of ions through six weighted densities instead of just one weighted density used in WDA.

The main approximation in FMT is the choice of the excess free energy for inhomogeneous fluids which is defined by

$$\beta F_{hs}^{ex}[\{\rho_j\}] = \int \Phi_{hs}^{ex}[\{\bar{\rho}_a(r)\}, \{\bar{\rho}_b(r)\}] d\mathbf{r}, \quad (\text{A1})$$

while the hard sphere one particle direct correlation function for inhomogeneous fluids can be obtained as usual by

$$c_i^{(1)hs}(r; \{\rho_j\}) = -\beta \frac{\delta F_{hs}^{ex}[\{\rho_j\}]}{\delta \rho_i(r)}, \quad i = 1 \dots m. \quad (\text{A2})$$

The corresponding expression for the homogeneous fluids $c_i^{(1)hs}(r; \{\rho_j^0\})$ can be subsequently obtained by replacing $\{\bar{\rho}_a(r)\} \rightarrow \{\xi_a\}$ into Eq. (A2) and by setting $\{\bar{\rho}_b(r)\} = 0$, where $a = 0, 1, 2, 3$, and $b = 1, 2$. The scaled-particle

variables ξ_a are defined as follows:

$$\begin{aligned}\xi_a &= \sum_{i=1}^m \rho_i^0 \mathcal{R}_i^a, \quad \mathcal{R}_i^0 = 1, \quad \mathcal{R}_i^1 = \sigma_i/2, \\ \mathcal{R}_i^2 &= \pi \sigma_i^2, \quad \mathcal{R}_i^3 = \pi \sigma_i^3/6, \\ \bar{\rho}_{3,i}(r) &= \frac{2\pi R_i}{r} \int_{|r-R_i|}^{r+R_i} dr' r' [R_i^2 - (r-r')^2] \rho_i^{(1)}(r') \\ &\quad + \Theta(R_i - r) 4\pi \int_0^{R_i-r} dr' r'^2 \rho_i^{(1)}(r') \\ \bar{\rho}_{2,i}(r) &= \frac{2\pi R_i}{r} \int_{|r-R_i|}^{r+R_i} dr' r' \rho_i^{(1)}(r'), \text{ and} \\ \bar{\rho}_{2,i}(r) &= \frac{\pi}{r^2} \int_{|r-R_i|}^{r+R_i} dr' r' (r^2 - r'^2 + R_i^2) \rho_i^{(1)}(r').\end{aligned}\quad (\text{A3})$$

Expressions for the scalar weighted densities $\bar{\rho}_{1,i}(r)$ and $\bar{\rho}_{0,i}(r)$ follow from $\bar{\rho}_{2,i}(r)$. Similarly, the expression for the vector weighted density $\bar{\rho}_{1,i}(r)$ follows from $\bar{\rho}_{2,i}(r)$.⁶⁰ The original version for $\Phi_{hs}^{ex}[\{\bar{\rho}_a(r)\}, \{\bar{\rho}_b(r)\}]$ proposed by Rosenfeld recovers Percus-Yevick (PY) equation of state (EOS)^{61,62} in the case of a homogeneous system. Improvements to FMT grouped under modified FMT (MFMT) recover more accurate equations of state in the uniform-fluid limit,^{44,45} including Carnahan–Starling (CS),⁶³ extended CS (eCS), and Boublik–Mansoori–Carnahan–Starling–Leland (BMC SL).⁶⁴ The inhomogeneous hard sphere excess free energy used in this study is based on the White Bear version of FMT mark II (WBFMT-II) recently introduced by Hansen-Goos *et al.*,⁴⁴ which recovers the Carnahan–Starling–Boublik equation of state in the uniform-fluid limit.^{44,65} Therefore, the use of WBFMT-II approximation in our theoretical formulation plays a fundamental role in properly and efficiently describing the effects of ionic asymmetry and solvent excluded volume on SEDLs, especially at high ion concentrations and size asymmetry ratios, where most of the aforementioned MFMT approximations deviate significantly from simulation results. More details on FMT and MFMT are given elsewhere.^{30,36,44–47}

2. Residual electrostatic correlation functions

The residual one particle correlation function for inhomogeneous fluids $c_{ij}^{(1)res}(r; \{\rho_j\})$ appearing in the argument of the exponential in Eq. (10) can be approximated by using a functional Taylor expansion at the first order in power of the ion density profiles around uniform fluids as

$$\Delta c_i^{(1)res}(r; \{\rho_j\}) = \sum_{j=1}^m \int d\mathbf{r}' c_{ij}^{(2)res}(\mathbf{r}, \mathbf{r}'; \{\rho_k^0\}) [\rho_j(\mathbf{r}') - \rho_j^0],$$

where the following relationship is used:

$$c_{ij}^{(2)res}(\mathbf{r}, \mathbf{r}'; \{\rho_k^0\}) = \left[\frac{\delta c_i^{(1)res}(r; \{\rho_k\})}{\delta \rho_i(r)} \right]_{\{\rho_k\}=\{\rho_k^0\}}.$$

The latter equation implies that $c_{ij}^{(2)res}(\mathbf{r}, \mathbf{r}'; \{\rho_k^0\}) = c_{ij}^{(2)}(\mathbf{r}, \mathbf{r}'; \{\rho_k^0\}) + z_i z_j e^2 / (\epsilon |\mathbf{r} - \mathbf{r}'|) - c_{ij}^{(2)hs}(\mathbf{r}, \mathbf{r}'; \{\rho_k^0\})$, where $c_{ij}^{(2)hs}(\mathbf{r}, \mathbf{r}'; \{\rho_k^0\})$ is the second order hard sphere correlation function. An explicit expression for the two particle correlation functions for multicomponent homogeneous fluids $c_{ij}^{(2)}(\mathbf{r}, \mathbf{r}'; \{\rho_k^0\}) \equiv c_{ij}^{(2)short-MSA}(\mathbf{r}, \mathbf{r}'; \{\rho_k^0\}) + c_{ij}^{(2)el-MSA}(\mathbf{r}, \mathbf{r}'; \{\rho_k^0\})$ was provided by Hiroike³⁸ using the MSA approximation.³⁷ The explicit expressions for $c_{ij}^{(2)el-MSA}(\mathbf{r}, \mathbf{r}'; \{\rho_k^0\})$ can be found in literature.^{30,31,38} For simplicity we assume that $c_{ij}^{(2)hs}(\mathbf{r}, \mathbf{r}'; \{\rho_k^0\}) \simeq c_{ij}^{(2)short-MSA}(\mathbf{r}, \mathbf{r}'; \{\rho_k^0\})$ in such a way that the residual one particle direct correlation function for inhomogeneous fluids can be calculated in terms of purely electrostatic contributions as

$$\begin{aligned}\Delta c_i^{(1)res}(r; \{\rho_j\}) &= \sum_{j=1}^m \int d\mathbf{r}' [c_{ij}^{(2)el-MSA}(\mathbf{r}, \mathbf{r}'; \{\rho_k^0\}) \\ &\quad + z_i z_j e^2 / (\epsilon |\mathbf{r} - \mathbf{r}'|)] [\rho_j(\mathbf{r}') - \rho_j^0].\end{aligned}\quad (\text{A4})$$

3. Computational scheme

The numerical solution of the coupled equations (10), (14), (A2), and (A4) used to calculate the ion density profiles is obtained iteratively using the Picard scheme, a simple but robust algorithm that combines simplicity and relative small memory requirements. Due to the presence of spherical symmetry, the properties of SEDLs only depend on the radial direction. We use a radial linear mesh with spacing h of the order 0.05–0.1 Å and number of grid points $N = 3000$. The well-known Debye-Huckel electrostatic potential approximation $\psi_{HD}(r, \{\rho_j\})$ is used as initial guess for the expression (14) which is replaced into the Eq. (9). The resulting values obtained for the ion density profiles $\{\rho_j(r)\}$ are replaced into Eqs. (A2), (A4), and (14). These expressions are subsequently replaced into Eq. (10) to generate the new guess for the ion profiles. This latter procedure is repeated until the difference between two consecutive values for the ion density profiles i and $i + 1$ satisfies the following tolerance criterion:

$$\frac{\sqrt{\sum_{l=1}^N \sum_{j=1}^m (\rho_j^{(i+1)}(r_l) - \rho_j^{(i)}(r_l))^2}}{Nm} < 10^{-6},$$

where $r_l = (l - 1) \cdot h + \text{Integer}[(R + \min\{\sigma_i\})/h]$. In order to moderate the iteration and to prevent the procedure from diverging, it is useful to mix the input profiles as follows:

$$\rho_j^{(i)}(r_l) \equiv \alpha \rho_j^{(i)}(r_l) + (1 - \alpha) \rho_j^{(i-1)}(r_l),$$

where α is a mixing parameter between zero and one. In the initial stages of iteration procedure, it is important to choose a value for α sufficiently small to prevent instabilities. In the later stages, α needs to be large enough to allow for fast convergence. A good performance is obtained using the following mixing parameter depending on the iteration number i :

$$\alpha(i) = 1 - \exp(-i/\lambda),$$

where λ is a real positive damping parameter that depends on the physical parameters of the system.

Overall, this algorithm provides solutions for the ion profiles in the order of 100 iterations and computing times between 10 to 60 s running the code on a single processor desktop computer. Better performance on the convergence and computing time may be obtained by using multigrid approaches and modified direct inversion in the iterative subspace (MDIIS) methods. We use the extended Simpson integral algorithm⁶⁶ to evaluate the radial integrals appearing in Eqs. (A3), (A1), and (A4). Alternatively, Fourier transforms may be used to improve efficiency if needed.⁶⁶

4. Grand canonical Monte Carlo simulations

Grand canonical Monte Carlo (GCMC) simulations are performed with the standard Metropolis algorithm to sample the distribution of ions in the electrolyte systems considered in this work. In the grand canonical ensemble, the number of each ion species in the system is allowed to fluctuate while keeping the chemical potentials of all the ion species constant. The temperature and volume of the system are also kept constant. The inhomogeneous electrolyte system containing the spherical macro-ion is considered to be in thermal and chemical equilibrium with the bulk homogeneous phase of the electrolyte solution where the electrostatic effects of the macro-ion are absent. The condition for chemical equilibrium is that chemical potential of each ion species is the same whether that ion species is in the inhomogeneous phase or in the bulk phase.

Sampling is achieved by random displacement, insertion, and deletion of individual ion species. In the insertion step, an ion species is randomly placed inside the simulation box, and in the deletion step, a randomly selected ion species is removed. The acceptance probabilities for inserting/deleting an ion species i , is defined by the following expression:^{67–69}

$$P_i^{\text{insert/delete}} = \min \left\{ 1, \frac{N_i!}{(N_i + \chi)!} V^\chi \exp \left(\frac{-\Delta\mathcal{U} + \chi\mu_i}{k_B T} \right) \right\}, \quad (\text{A5})$$

where N_i is the number of ion species i before the insertion/deletion, μ_i is the chemical potential of ion species i , V is the volume of the simulation box ($V = L^3$), $\chi = 1$ for insertion and -1 for deletion, k_B is the Boltzmann's constant, and $\Delta\mathcal{U}$ is the free energy change associated with the insertion/deletion step. To run the GCMC simulations, the chemical potential of each ion species (μ_i) has to be known. Since the system is in thermal and chemical equilibrium with the bulk homogeneous phase of the electrolyte solution, the chemical potential of each ion species in the system is set equal to the ion species' bulk chemical potential. In this work, the bulk chemical potential is parameterized by computation for a fixed bulk concentration of the ion species (at $T = 298$ K, $\epsilon = 78.54$) using the iterative charge corrected adaptive GCMC algorithm developed by Malasias and Boda.⁶⁷ In the displacement step, an ion is randomly selected and displaced. The displacement is accepted with a probability,

$$P_i^{\text{displ}} = \min \{ 1, \exp(-\Delta\mathcal{U}/k_B T) \}. \quad (\text{A6})$$

$\Delta\mathcal{U}$ in Eq. (A6) is the free energy change associated with the random displacement of an ion.

Since the number of each ion species fluctuates at each step of the GCMC simulation, the total charge in the system also fluctuates at each step, and the system is electrically neutral only on average. Each GCMC step can be an attempt to randomly insert, delete, or displace an ion. Roughly about 50%-70% of the MC steps are single-ion displacement attempts. The rest of the MC steps are split between the insertion and deletion attempts with equal probability. The statistics for calculating the ion density profiles are obtained as follows: First, the simulation is run for 10^8 MC steps, starting with a random configuration (state) of the ions in the simulation box. The simulation is repeated eight times, starting with different equilibrium configurations of the system obtained from the last 30% steps of the first simulation. The statistics of the ion distributions from all the steps of the eight independent GCMC simulations are then used to compute average ion density profiles of each ion species around the spherical macro-ion. Each of the eight simulations is run for 10^8 steps. The GCMC simulations are performed only for validating the DFT results associated with PM and RPM models, whereas, for SPM model we use MC simulations from Patra's paper.⁴⁰

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