



Review

Size and/or charge asymmetry effects in coulombic fluids in the presence of external fields: From simple electrolytes to molten salts

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ABSTRACT

Charged fluids are ubiquitous in biology and in everyday products such as milk, cosmetics, lubricants, paints, or drugs. The stability and aggregation of charged colloidal solutions are of outstanding relevance in nature and in diverse biomedical applications, including the fabrication of photonic materials and scaffolds for biological assemblies, gene therapy, diagnostics, targeted drug delivery, and molecular labeling. When an electrode or a charged colloidal particle is immersed in a Coulombic fluid, an ionic cloud or electrical double layer forms. One of the most simple theoretical descriptions of the electrical double layer can be provided via the non-linear Poisson-Boltzmann theory of point-ions. In planar geometry, it is possible to derive an analytical description of the electrical double layer for $z : z$ electrolytes. In spite of its simplicity, this mean field approach neglects important characteristics of charged fluids such as ion correlations, ionic excluded volume, polarization effects, etc. Thus, in this review article I would like to discuss some consequences of breaking the symmetry in the ionic size and/or valence of charged fluids in the presence of an external field when ion correlations and ionic excluded volume effects are included consistently. The external field can be produced by a charged electrode or an electrified colloidal particle, and the associated electrical double layer is studied via integral equations theory, and/or molecular simulations beyond the classical non-linear Poisson Boltzmann theory of point ions.

1. Introduction

Coulombic fluids are ubiquitous in biological systems, just consider water molecules, ions and charged biomolecules in living beings as an example. Coulombic fluids are also common in daily products such as milk, cosmetics, lubricants, paints, and drugs. In addition, colloidal suspensions of macroions have been shown to be ideal for the fabrication of photonic materials and scaffolds for biological assemblies, gene therapy, diagnostics, targeted drug delivery, and molecular labeling [1–4]. Additional examples of Coulombic fluids are molten salts, ionic liquids, and liquid metals. These charged fluids have relevant applications in the fabrication of very efficient devices to store electricity such as novel batteries and/or supercapacitors [5].

If a charged electrode or a macroion is immersed in a Coulombic fluid, it is possible to observe a diffuse ionic cloud or electrical double layer. The electrostatic and thermodynamic properties of charged colloids, such as macroions, charged biomolecules, or electrified electrodes immersed in an Coulombic fluid are mainly determined by the spatial distribution of ions or the associated electrical double layer. A large

number of experimental, theoretical, and simulation works have been performed since the last century in order to understand the microscopic and macroscopic properties of the electrical double layer in a wide variety of conditions [6,7]. This knowledge is very important to comprehend complex physicochemical and biological processes, and to propose novel technological applications based on charged soft condensed matter.

One of the most simple theoretical frameworks to model the electrical double layer is based in the non-linear Poisson-Boltzmann theory of point ions. In fact, it is possible to derive an analytical description of the electrical double layer for $z : z$ electrolytes in planar geometry [8]. In spite of its simplicity, this mean field approach neglects important characteristics of charged fluids such as ion correlations, ionic excluded effects, polarization effects, etc. In addition, this mean field analytical description of $z : z$ electrolytes imposes a symmetry in the ionic size (at the level of the ionic closest approach distance of ions to the charged surface) and in the valence of the ionic species. In nature, ions may have different valences. Moreover, ions in aqueous electrolytes are usually solvated by different layers of water molecules. As a result, ionic species

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are not equally-sized or size-symmetric in general. On the other hand, several authors have emphasized the role of counterions suggesting that the role of coions is irrelevant. In particular, almost 40 years ago Valleau and Torrie performed a theoretical prescription, in the non-linear Poisson-Boltzmann framework, about the role of the ionic size-asymmetry in the electrolytic charge distribution of a binary mixture of valence-symmetric *semi-point* ions, next to a charged plane. In that study [9], they pointed out an apparently “obvious” or expected fact later known as the dominance of the counterions in the electrical double layer. According to them, only counterions are found near the surface of a strongly charged colloid of either sign. Thus, in the limit of very strong electric fields, the ionic size-asymmetry between coions and counterions becomes irrelevant and the only important ion-size parameter is the effective radius of the counterions. In other words, and quoting those authors: “...When there is a substantial surface charge...we expect the double layer properties of a dilute electrolyte to become similar to those of a completely symmetric electrolyte having an effective size equal to that of the counterion...”. In such a scenario, the contribution of coions to the properties of the diffuse electrical double layer becomes negligible regarding the contribution of counterions. As a result, the properties and behaviour of coions at large electric fields are irrelevant in this classic description of the electrical double layer, whose characteristics are dominated or determined mainly by counterions. This mean field recipe led to many researchers to unfofoundedly extend its validity to the case of genuine hard-sphere ions of arbitrary size and valence close to a charged surface [10–20], which corresponds to the so-called “unrestricted” primitive model of the electrical double layer. The direct application of the dominance principle, stated by Valleau and Torrie exclusively in the non-linear Poisson-Boltzmann formalism, to the primitive model of colloidal systems is neither appropriate nor justified when ion correlations and ionic excluded volume effects are relevant.

Thus, in this article I would like to review some consequences of breaking the symmetry in the ionic size and/or valence of charged fluids in the presence of an external field produced by either a charged electrode or an electrified colloidal particle beyond the classical non-linear Poisson Boltzmann theory. This has been performed via integral equations theory and/or molecular simulations in the so-called primitive model, which will be described in the following section.

2. Model, theory, and simulations

Let us start by considering a point-ions $m : n$ electrolyte bathing a charged and infinite planar electrode with a positive bare surface charge density σ_0 . Anions (counterions) and cations (coions) can approach up to the colloidal surface, where the surface mean electrostatic is Ψ_0 (see Fig. 1). The non-linear Poisson-Boltzmann equation for the local mean electrostatic potential can be expressed in terms of the ionic profiles next to the charged electrode. In such a scenario, the normalized ionic profile $g_i(x)$ of the species i in planar geometry is related, in general, to the ionic

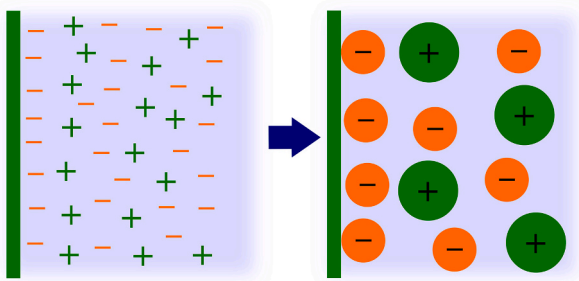


Fig. 1. Color online: Point ions model (left) used in the non-linear Poisson Boltzmann theory, and primitive model (right) used in the integral equations theory as well as in Monte Carlo and molecular dynamics simulations in planar geometry.

potential of mean force $W_i(x)$ as:

$$\rho_i(x) = \rho_i^{bulk} g_i(x) = \rho_i^{bulk} e^{-W_i(x)/k_B T}, \quad (1)$$

where k_B is the Boltzmann constant and T is the absolute temperature of the system. The potential of mean force is the necessary work required to bring a charged particle from infinite up to a distance x , where x is the perpendicular distance between a point in the three-dimensional space and the surface of the electrode. As a first approximation, the potential of mean force can be equated to the electrostatic energy $W_i(x) = e_0 z_i \Psi(x)$, where e_0 is the protonic elementary charge, z_i is the valence of ions of species i and $\Psi(x)$ is the mean electrostatic potential due to the charged surface and the electrolyte. If the ionic profiles, defined in terms of the mean electrostatic potential, are substituted in the Poisson equation, $\nabla^2 \Psi(x) = -\rho_{el}(x)/(\epsilon_0 \epsilon)$, then the non-linear Poisson-Boltzmann equation is obtained

$$\nabla^2 \Psi(x) = -\frac{1}{\epsilon_0 \epsilon} \sum_i \rho_i^{bulk} z_i e_0 \exp\left(-\frac{e_0 z_i \Psi(x)}{k_B T}\right). \quad (2)$$

The linear Poisson-Boltzmann equation can be obtained by linearizing Eq. (2). For a charge symmetric $z_- : z_+$ electrolyte (with $z_- = -z_+$) this linear approximation results in the following relation between the mean electrostatic potential at the electrode's surface Ψ_0 , and the surface charge density σ_0

$$\Psi_0 = \frac{\sigma_0}{\epsilon_0 \epsilon \kappa_D} \quad (3)$$

in planar geometry. In this definition, the Debye length of the supporting electrolyte in bulk is defined as $\lambda_D = 1/\kappa_D$ with

$$\kappa_D = \left(\frac{\sum_i \rho_i^{bulk} z_i^2 e_0^2}{\epsilon_0 \epsilon k_B T} \right)^{\frac{1}{2}}. \quad (4)$$

Additionally, the corresponding integrated charge, electric field, and mean electrostatic potential for the planar instance can be written, in general, as [21]

$$\sigma(x) = \sigma_0 + \int_0^x \sum_i \rho_i^{bulk} g_i(t) e_0 z_i dt, \quad (5)$$

$$E(x) = \frac{\sigma(x)}{\epsilon_0 \epsilon}, \quad (6)$$

and

$$\Psi(x) = \frac{e_0}{\epsilon_0 \epsilon} \int_x^\infty (x-t) \left(\sum_{i=-,+} \rho_i^{bulk} z_i (g_i(t) - 1) \right) dt. \quad (7)$$

One alternative to provide a theoretical description of the electrical double layer beyond the mean-field non-linear Poisson-Boltzmann theory is via integral equations theory. In such a scenario, ionic species are modelled in the so-called primitive model. In this approach, ionic species are considered point charges embedded in hard spheres of radius r_i . As a result, ion correlations and ionic excluded volume effects are consistently incorporated in this approach. The Ornstein-Zernike equations describing the ionic cloud around a single spherical macroion can be written as

$$h_{Mj}(r) = c_{Mj}(r) + \sum_{k=-,+} \rho_k \int h_{Mk}(t) c_{kj}(|\vec{r} - \vec{t}|) dV, \quad (8)$$

for $j = +, -$, and where $h_{Mj}(r) = g_{Mj}(r) - 1$ are the total ionic correlation functions, and $g_{Mj}(r)$ are the ionic radial distribution functions. Note that, since here we are considering the particular case of the Ornstein-Zernike equations for a spherical colloid, there are not angular dependencies in all the involved functions. The direct correlation functions between ions and the spherical colloid are specified by using the

hypernetted-chain (HNC) closure $c_{Mj}(r) = -\beta U_{Mj}(r) + h_{Mj}(r) - \ln [h_{Mj}(r) + 1]$. If $c_{kj}(|\vec{r} - \vec{r}'|) = -\beta(z_k z_j e_0^2) / (4\pi\epsilon_0\epsilon |\vec{r} - \vec{r}'|)$ is employed in the right-hand side of Eq. (8), the integral equations version of the non-linear Poisson-Boltzmann theory is then obtained [22]. The integral form of the non-linear Poisson Boltzmann equation for the electric double layer of a binary electrolyte next to a planar charged surface can be obtained from Eq. (8) by taking the limit of a colloid with infinite radius [23]. These equations can be explicitly written as

$$g_i(x) = \exp \left\{ -z_i e_0 \beta \Psi_0 - z_i \left(\frac{e_0^2}{k_B T \epsilon_0 \epsilon} \right) \int_b^\infty \left[\sum_j z_j \rho_j g_j(t) \right] \mathcal{F}(xt) dt \right\}, \quad (9)$$

for $x \geq 0$, $i, j = +, -, \text{ and}$

$$\mathcal{F}(x, t) = \frac{(x+t) - |x-t|}{2}. \quad (10)$$

Analogous expressions for cylindrical and spherical geometries, in the absence of polarization effects, can be found elsewhere [21,23,24]. Monte Carlo and/or molecular dynamics simulations in the primitive model have been also performed in several instances to test the accuracy of integral equations results [21,23,25–31] and classical density functional theory [32–43]. On the other hand, integral equations theory has been also used to explain, from first principles and in the absence of specific ionic adsorption effects, the local inversion of the mean electrostatic potential near the surface of DNA macromolecules and planar membranes [24,38,39,44] by taking into account ion correlations and ionic excluded volume effects. The osmotic pressure and the Donnan equilibrium in aqueous protein solutions of human and bovine serum albumin have been also studied via integral equations theory [45].

3. On the dominance and the non-dominance of counterions in the electrical double layer

As it was mentioned in the introduction, according to Valleau and Torrie, in the limit of very strong electric fields, the ionic size-asymmetry between coions and counterions becomes irrelevant and the only important ion-size parameter is the effective radius of the counterions. In a very recent work [48], it has been explicitly shown, via analytical and numerical calculations, that the electrical properties associated to the surface of a planar electrode next to a $1 : z$ electrolyte, such as the surface mean electrostatic potential Ψ_0 or the capacitive compactness $\tau_c(\Psi_0, \sigma_0)$, exactly fulfill the Valleau and Torrie's prescription of the dominance of counterions in the non-linear Poisson-Boltzmann theory. However, in the same work it was shown that, in general, the counterions do not necessarily dominate in the planar electrical double layer at the level of electrostatic properties such as the local mean electrostatic potential $\Psi_0(x)$ and the electric field $E(x)$ in the whole space, that is, in the limit of an infinite surface charge density it was evinced, via analytical and accurate numerical calculations, that, according to the non-linear Poisson-Boltzmann picture, the $\Psi(x)$ and $E(x)$ do not converge uniformly in the whole space to the same value in the presence of $1 : z$ electrolytes, even if the properties of monovalent counterions are the same. These results are consistent with primitive model Monte Carlo simulation data at large bare surface charge densities [21,48]. The qualitative agreement displayed by the non-linear Poisson-Boltzmann theory regarding the primitive model Monte Carlo simulations is probably due to the fact that the bulk $1 : z$ electrolyte with monovalent counterions is still in the weak electrostatic coupling regime, despite the increase of the corresponding ionic strength as a function of the valence z of the multivalent coions, when the properties of counterions are fixed.

On the other hand, when ion correlations and excluded volume effects are included, it has been shown that the counterions do not dominate or determine the properties of the primitive model electrical double layer in the whole space [25,26]. In these articles it was found that, at large colloidal charges, the behaviour of the primitive model electrical double layer associated to a $z : z$ size-asymmetric electrolyte

does not converge to that of a $z : z$ size-symmetric electrolyte when the properties of counterions (such as the ionic size, valence, and concentration) are the same in both electrolytes. In other words, in such articles it has been proved that the characteristics of the coions in $z : z$ electrolytes, symmetric in valence and asymmetric in size, are relevant and do matter for highly electrified colloids at high salt concentrations. Afterwards, it was shown that in the case of equisized $1 : z$ primitive model electrolytes with multivalent coions [27], the properties of the electric double layer do not converge in the limit of very large colloidal surface charge densities (as it would be expected according to the dominance of counterions in the classical non-linear Poisson-Boltzmann approach). That is, it has been explicitly shown that, for equally-sized $1 : z$ primitive model electrolytes, counterions do not dominate the properties of the ionic cloud around highly charged colloids when ion correlations and ionic excluded effects are taken into account consistently. These ingredients are missing in classical mean field descriptions, such as the non-linear Poisson-Boltzmann theory.

4. Ionic liquid-state diode and negative differential conductance in biological systems

In addition to the breaking of the symmetry of the ionic size and valence in Coulombic fluids, another interesting effects can be observed in mixtures of ions with different solvation energies near the interface between two immiscible electrolyte solutions. Let us consider two immiscible solvents in contact, such as oil and water. The oil/water interface is one of the most simple models mimicking a cellular lipid membrane in contact with an aqueous electrolyte solution. The ionic solvation energy is the energy necessary to transfer an ion from a solvent (e.g., water) to the other solvent (e.g., oil) [49]. In the case of a binary electrolyte, the ionic solvation energy allow us to observe the phenomenon of ion partitioning. In order to define this behaviour, let us suppose that the electrolyte is placed initially in one medium. Depending on the solvation energies of the ionic species, it is possible to observe a transfer of ions from one medium to the other one. As a result, an electrical double layer is formed at the interface between the two solvents, and two different bulk concentrations can be observed in each solvent medium. This is the so-called ion partitioning [49]. In the presence of four species, with different but appropriate ionic solvation energies, it is possible to observe a preferential transfer of ions depending on the direction of an applied electric field: in one direction the electric field produces a current that is significantly larger in comparison with the magnitude of the same quantity when the electric field is applied in the opposite direction. This phenomenon resembles to the behaviour of the electric current in a typical solid state diode. An asymmetric ion transfer at the interface between two immiscible liquids has been observed experimentally at the water/nitrobenzene interface in the presence of tetrabutylammonium perchlorate and tetraethylammonium bromide. This system has been theoretically modelled via the non-linear Poisson-Boltzmann theory and Monte Carlo simulations including polarization effects, which are produced by the dielectric contrast between the water and the nitrobenzene solvents, and taking into account the experimental ionic solvation energies consistently [50]. In such a scenario, it is remarkable that the non-linear Poisson-Boltzmann theory be able to predict qualitatively the asymmetry in the number of carriers, as a function of the direction and magnitude of an applied electric field, observed in Monte Carlo simulations. These simulations include ion correlations and ionic excluded volume effects, which are present in the corresponding experimental system. Nevertheless, it is important to mention that the number of carriers predicted by the non-linear Poisson-Boltzmann theory is overestimated regarding Monte Carlo simulations, which emphasizes the relevance of ion correlations and ionic excluded volume and polarization effects.

On the other hand, in addition to the experimental asymmetric time-dependent electric current behaviour observed as a function of the voltage bias applied to the above water/nitrobenzene interface, a

negative derivative of the current as a function of the voltage bias has been also observed. That is, experiments have shown a negative differential conductivity at large enough positive voltage bias values (see, e.g., Fig. 1 of Ref. [50]). This behaviour is more conspicuous at slow scanning rates. Moreover, an increase in the initial concentration of all supporting electrolytes produces a shift in the onset of the negative slope conductance to lower voltage bias. Negative differential conductance (or negative resistance) has been observed experimentally in several fields, including solid-state electronics and neurobiology. This property is the basis of several electric semiconductor rectifiers such as tunnel or Gunn diodes [51], which are used typically in high-frequency oscillators. In the context of biological membranes, steady-state negative conductances have been reported in several current-voltage studies of squid giant axons since the 1950s using voltage clamp techniques [52]. Modern patch-clamp studies have also reported the existence of negative slope conductance in brain and heart cells [53–62]. It has been suggested that a negative conductance is typical in regenerative phenomena, excitation threshold, and repetitive activity of neurons at a physiological level [55,63,64]. In the context of a simple electrolyte liquid interface, current-voltage measurements display many features already observed in more complex biological counterparts, namely, the appearance of a voltage region in which the electric current decreases when a voltage bias increases (after a critical value) producing a negative slope conductance, or a shift in the onset of negative slope conductance as a function of the salt concentration [59]. The negative conductance observed in the experiments reported in Ref. [50] is likely produced by an ion crowding effect promoting the appearance of a dynamic energy barrier at the liquid interface.

5. Charge inversion, charge reversal, surface charge amplification, and enhancing and inversion of the electric field at an oil/water interface

An ionic cloud or electrical double layer forms near a charged electrode or electrified macroion immersed in a Coulombic fluid. As a result, ions with opposite sign regarding the colloidal surface charge density, or counterions, tend to be in excess near the charged surface; whereas ions with the same sign regarding the colloidal surface charge density, or coions, tend to be in deficit near the charged surface. When the role of counterions and coions is inverted, the phenomenon of charge inversion appears. As a result, the net charge of the electrode and the ionic species can invert its sign. This behaviour is the so-called charge reversal [28]. Charge reversal has been observed experimentally in biochemical systems in the presence of protein-coated Au nanoparticles caused by the addition of metal ions [65], as well as near a supported lipid bilayer carrying a slight negative charge that was used as an idealized model of a biological membrane at which a cationic polyelectrolyte was adsorbed [66]. Another interesting behaviour that appears in the presence of ionic size asymmetry is the so-called surface charge amplification [28]. When two ionic species have different closest approach distances to a colloidal surface, there is a spatial region in which only the smallest ionic species can enter. In particular, let us consider a binary size-asymmetric electrolyte. If the colloidal charge is not very large and the coions are the smallest species it is possible to observe an increase of the net or integrated charge near the colloidal surface. This is the so-called charge amplification. In addition, if the colloidal charge is not very large and the counterions are the smallest species it is possible to observe an inversion of the net or integrated charge near the colloidal surface, which corresponds to the phenomenon of charge reversal. In the presence of oil/water interfaces, the ionic size asymmetry including polarization effects can induce an enhancement or an inversion of the electric field near the oil/water interface depending on the direction of the applied electric field [46,47].

On the other hand, the phenomenon of charge reversal can be also promoted by ion correlations and ionic excluded volume effects in equally-sized electrolytes neglecting polarization effects [23,25–28,67].

In the presence of polarization or image charge effects, it is possible to observe the phenomenon of charge amplification in the presence of 1 : z electrolytes surrounding a spherical macroion. That is, image charge effects are able to induce an effective ionic-size asymmetry in the presence of multivalent counterions if polarization effects are taken into account. Physically, this occurs because the image charge auto-repulsion can overcome the attraction of multivalent (e.g., trivalent) counterions in the presence of a dielectric macroion with dielectric constant lower than that of the solvent (e.g., 2 for polystyrene and 78.5 for water) [67].

6. Expansion and shrinkage of the electrical double layer in the presence of an external electric field

The spatial extension or thickness of the electrical double layer surrounding a charged colloid is a measure of the neutralization of the bare or native colloidal charge, and determines the colloidal stability properties of these macroparticles in solution. In particular, it has been shown that the electrical double layer can experience a peculiar expansion and shrinking in the presence of valence-asymmetric molten salts and simple charge-asymmetric electrolytes if coions are multivalent [21,23]. This observation has been performed via simulation and theory by calculating the *capacitive compactness* of the electrical double layer [21,23,29], which is a generalization of the Debye length of the supporting electrolyte in bulk, which is defined as $\lambda_D = 1/\kappa_D$.

The concept of the capacitive compactness or compactness was proposed for the first time by González-Tovar et al. in 2004 in spherical geometry [29]. By considering the global electroneutrality of an electrode-electrolyte system, it is possible to replace the real system by an effective capacitor, in which the diffuse electrical double layer charge is placed in an electrode with a charge equal in magnitude to that of the real solid electrode but with opposite sign. The distance from the coordinate origin at which this electrode is located is, precisely, the capacitive compactness [21,23,29]. Note that, if the location of the electrical double layer electrode is measured from the surface of the real solid electrode, then the capacitive compactness can be also interpreted as the separation distance between both electrodes. In the literature, it is very well known that the Debye length, and the associated electrical double layer, shrinks as a function of the ionic strength of the supporting electrolyte. However, the Debye length cannot take into account the influence of the surface charge density of the electrode, as well as other relevant properties of Coulombic fluids such as ion correlations, ionic excluded volume effects, polarization effects, ionic specific adsorption, etc. In this sense, the capacitive compactness is a generalization of the Debye length that has proven to be very useful to quantify the thickness or spatial extent of the ionic cloud neutralizing a charged surface. By using general electrostatics and a normalized net charge density weight function [68], it has been shown that the corresponding expected value of the electrostatic potential $V(\vec{r})$ produced by an electrode in planar, spherical, and cylindrical geometries immersed in a continuum solvent in the absence of small charged particles, i.e., the bare electrostatic potential due to the electrode, is equal to i) the negative of the mean electrostatic potential Ψ_0 at the surface of an electrode immersed in a charged fluid with net charge density $\rho_c(\vec{r})$ and the same surface charge density σ_0 , and also ii) to the bare electrostatic potential evaluated at the centroid of charge of the supporting Coulombic fluid (which is the so-called capacitive compactness of the electrical double layer). As a direct application of these results, alternative explicit expressions of the capacitive compactness have been provided as the expected value of functions that depend on the specific geometry of the electrode [68].

7. Like-charge attraction and enhanced electrostatic repulsion between equally charged macroions in the presence of size- and/or charge-asymmetric aqueous electrolytes

An asymmetric charge neutralization and electrostatic screening

depending on the charge polarity of a single nanoparticle can occur in the presence of a size-asymmetric monovalent electrolyte. A possible path to observe the consequences of such a behaviour in non-concentrated solutions of macroions is by studying the potential of mean force between two macroions in similar conditions. In particular, at high electrolyte concentrations, it has been shown that small monovalent counterions and large coions are able to promote a short like-charge attraction [30]. Physically, small ions allow a “bridging” between two equally-charged macroions. On the contrary, in the presence of large counterions and small coions it has been observed an enhancement of the repulsion between two equally-charged macroions regarding the classical DLVO theory. This last behaviour has been experimentally observed in suspensions of macroions immersed in large tetraalkylammonium salts, and it has been modelled via integral equations theory and MD simulations at the level of the potential of mean force between two equally charged macroions in the primitive model [31].

On the other hand, a long range like-charge attraction has been observed experimentally between equally charged nanoparticles [69]. Specifically, *Au* nanoparticles were coated with noncomplementary DNA designed to prevent interparticle assembly via Watson-Crick hybridization. Small-angle X-ray scattering (SAXS) measurements have shown that these highly charged nanoparticles undergo “gas” to face-centered cubic (FCC) to “glass-like” transitions with increasing the electrolyte concentration of size- and/or valence-asymmetric *NaCl* or *CaCl₂* salts. Molecular dynamics simulations have revealed that the crystallization is concomitant with interparticle interactions changing from purely repulsive to a “long range potential well” condition, which can be explained as a sum of cohesive and depletion forces that originated from the inter-electrolyte ion and electrolyte-ion-nanoparticle positional correlations [69].

8. Concluding remarks

In this article, several instances have been discussed in which the breaking of the symmetry in the ionic size and valence can promote interesting phenomena such as charge inversion, charge reversal, charge amplification, enhancing and inversion of the electric field near an oil/water interface, like-charge attraction, and an enhancement of the repulsion between like-charged colloidal particles. In particular, the importance of the properties of coions in the presence of salts in which counterions have the same properties at large electric fields, that is, the non-dominance of counterions in the 3D space, has been discussed in the non-linear Poisson-Boltzmann theory, integral equations theories, and Monte Carlo and molecular dynamics simulations. Polarization effects have been shown to be able to induce an effective ionic size-asymmetry in the presence of equally sized electrolytes with multivalent counterions, promoting the occurrence of the charge amplification phenomenon. An exciting phenomenon related to mixtures of electrolytes with different ionic solvation energies near oil/water interfaces, in the presence of an applied external electric field, is the possibility of building a liquid-state diode.

One important advantage of using the primitive model, in the theoretical description provided by integral equations theory and Monte Carlo and molecular dynamics simulations to describe the asymmetry in Coulombic fluids, is that allow us to study simplified biophysical systems at low ion concentrations including ion correlations and ionic excluded effects consistently from first principles. These features can promote interesting phenomena such as charge inversion, charge reversal, surface charge amplification, etc., which are absent in the classical non-linear Poisson-Boltzmann picture. On the other hand, a relevant limitation of the primitive model is that the solvent is incorporated as a continuum medium. As a result, the granularity and the dipolar moment of the solvent are ignored. A more realistic modelling of the influence of the ionic size- and valence-asymmetry in the electrical double layer of Coulombic fluids, beyond the primitive model, could

include the characteristics of the solvent, polarization effects, specific ionic adsorption, etc.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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