Lattice-gas Poisson-Boltzmann approach for sterically asymmetric electrolytes

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We derive a modification of the Poisson-Boltzmann (PB) equation brought about by the finite and different sizes of mobile ions. The equation we obtain contains explicitly the size asymmetry of the electrolyte, enabling one to apply the PB approach to the cases where this effect may be of importance. We show that the modification we propose predicts the asymmetry of the double-layer capacitance. Our approach thus provides a transparent analytical framework for a previously proposed heuristic modification of the PB equation, which also predicts the same effect. In addition, a detailed exposition of the lattice-based calculation of the entropy, accounting for steric, spatial correlations, enables us to clearly pinpoint some of the drawbacks of such an approach, which are not entirely obvious in previous attempts to include the steric effects in the PB equation.

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I. INTRODUCTION

Although of a mean-field nature, the Poisson-Boltzmann (PB) approach has proven its value in explaining electrostatic interactions in very different systems (see, e.g., Refs. [1–4]). The approach is known, however, to break down in situations where the ionic correlations are of importance, and this is particularly the case for strongly charged (with valencies three and larger) mobile (screening) ions [5,6]. The mobile ions in the PB approach are treated as an ideal gas which interacts with the external electrostatic potential, but also modifies its spatial dependence as it changes concentration—this is the essence of the mean-field idea behind the PB scheme. However, even such a scheme often needs to be additionally simplified in order to yield solvable equations. An important simplification which is typically applied in combination with the mean-field approximation is the assumption of the vanishing *size* of the ions. This assumption may be problematic in cases when the solution contains objects (e.g., plates, macromolecules, etc.) with large (surface) charge densities. A large quantity of mobile charge is needed to efficiently screen such static charges, which may result in a buildup of large ionic concentrations in the spatial regions close to the strongly charged objects. In such cases, the results predicted by the PB equation, in combination with the assumption of vanishing ionic size, may be in conflict with the maximum concentration achievable by ions with finite radius R, which is of the order of $\sim 1/R^3$. Thus, due to steric effects only, electrostatic screening becomes less efficient as the ionic radius increases, i.e., the maximum achievable ionic concentrations decrease. Alternatively, the effect of the steric hindrance of ions may be prominent even for small charge densities, when the sizes of the ions are very large—such a situation may be of importance in studies of the adsorption of proteins on charged nanoparticles, when the proteins are treated as screening "ions" [7].

To properly assess the utility of the PB approach, before abandoning it in favor of more complicated schemes, one needs to first examine whether some of its apparent drawbacks (see, e.g., Ref. [8]) can be related to effects which are not related to its mean-field origin. Steric constraints on the mobile ion concentrations are such an effect, already identified in the existing literature. Various authors have attempted to include steric ionic effects in electrostatic formalisms of a different nature [9–14]. An overview of the modifications of the Poisson-Boltzmann equation to include the finite size of ions can be found in Ref. [15]. These attempts and modifications have a long history, starting with the work of Stern [16] in 1924, and gaining momentum with the paper by Bikerman in 1942 [15,17].

However, most of the previous work assumed that ions are of the *same size* (but not all—see Refs. [18–21]). While this may be sufficient for most cases, the ionic size asymmetry may be important, e.g., in ionic transport across membrane channels (see, e.g., Ref. [22]), and, generally, in all cases where the charged objects have geometrical features, such as holes, pores, and indentations, comparable to the (largest) ionic size—the systems which come to mind are supercapacitors with subnanometer sized pores [23]. In particular, the steric asymmetry of the electrolyte needs to be accounted for in order to reproduce the asymmetric, double-humped shape of the double-layer capacitance, which was measured in room temperature ionic liquid systems and explained by numerical simulations [24]. The modification of the PB approach we propose explains the occurrence of the same effect in aqueous electrolytes [25].

One may wonder about the need for yet another modification of the PB equation to account for the effects of the size of ions. Indeed, one may think of using one of the previous schemes derived for one type of counterion only, or for anions and cations of the same size, and apply them separately to the regions of positive and negative charges, "superposing" the results in the end. Even if somewhat clumsy, such a scheme could be of use in parallel plate geometry, but it is certain to fail when there are more complicated spatial distributions of charge, such as in the case of proteins or protein quaternary structures [2–4]. In such cases, it would be of use to have a modification of the PB differential equation, accounting for the effect of interest which could be, for example, implemented in existing numerical PB solvers [4]. Our approach produces such a modification. An important previous attempt to consistently account for the effects we are interested in has been reported in Ref. [19]. The authors combine the analytical expression for mixing entropy for hard spheres of unequal size and combine it with the Poisson equation [19]. This produces a self-consistent scheme which needs to be implemented numerically [see also Ref. [20]

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which also provides a (different) numerical scheme for the problem of interest]. Our approach is different in spirit, and its final result is an *analytical* modification of the PB differential equation. This should be advantageous because it allows for the application of powerful numerical methods (see, e.g., Ref. [4]).

The sterically modified PB approach by Borukhov *et al.* [12] is of particular interest to us. Chu *et al.* [21] have made a simple extension of this approach [12] by allowing several ions to be in one lattice cell. Kornyshev [8] has semiempirically extended the sterically modified PB equation, obtained along similar lines to those in Ref. [12], to the case of an asymmetric salt. Our aim in this paper is to rigorously extend the work of Borukhov *et al.* [12] so as to consistently account for the situation in which the *sizes of the mobile ions are not the same*, which is typically the case. In addition, we intend to clearly expose all the subtleties of the modification of the PB approach and identify potentially problematic issues. Unlike some previous modifications, our approach does not rely on the underlying lattice, and our equations have a clear continuum limit (when the lattice parameter vanishes).

Steric effects are most easily included in the PB framework in a lattice counting scheme—this is also in the background of the Borukhov *et al.* approach. Our modification of the scheme will be to consider the ions whose linear dimension is an integer number of times bigger than the lattice cell size a. We shall show that this procedure allows one to study the limit in which the lattice cell size vanishes, $a \to 0$, recovering in such a way the true continuum description.

II. DERIVATION OF THE MODIFIED PB EQUATION

We shall consider a symmetric $z:z$ electrolyte. The general, mean-field flavored free energy is given by

$$F = \int d\mathbf{r}\left\{-\frac{\epsilon}{2}|\nabla\psi|^2 + \psi ez(c_+ - c_-) - \mu_+ c_+ - \mu_- c_- - Ts\right\}, \quad (1)$$

where T is temperature and s is the entropy density. We now inspect a small volume of the electrolyte containing N cells (of linear dimension a) in which the ionic concentrations, c_+ and c_-, and potential ψ are approximately constant. The entropy contribution can be obtained as the logarithm of the number of configurations (W) representing $N_+ = c_+ N a^3$ positive and $N_- = c_- N a^3$ negative ions in N cells. Each ion occupies a cube of size $L_+ a$ ($L_- a$), where L_+ (L_-) is an integer. If $L_+ = L_- = 1$, we can recover the Borukhov *et al.* result [12], while Chu *et al.* [21] have studied the case when multiple ions can be put in one cell. Here we study the case when ions occupy more than one cell ($L_+, L_- > 1$).

An L_+-sized ion excludes $(2L_+ - 1)^3$ cells for other L_+-sized ions and $(L_+ + L_- - 1)^3$ cells for ions of size L_- (see Fig. 1). This assumption is what we use, although it is true only for sufficiently small concentrations, as two ions that are close can share the volume they effectively exclude. Thus, the excluded volume per ion is smaller than predicted for that case—in the extreme limit when all cells are occupied with ions, each of them fills the volume equal to its size, i.e., their excluded volume is equal to their volume. Thus, in passing from low- to high-density ionic configurations, the effectively "excluded volume" should thus decrease, and one should keep this in mind. Stated somewhat differently, the assumptions underlying the calculation of entropy in the low-density regime become invalid in the regime of high ionic densities and the type of spatial correlations induced by steric hindrance importantly changes. To further illustrate this effect, we performed numerical simulations on a system of identical hard spheres (particles). In Fig. 2 we show the volume available for the insertion of an additional particle (v_a) as a function of the number of particles (N) present in the simulation box. The simple account of steric effects predicts that the volume

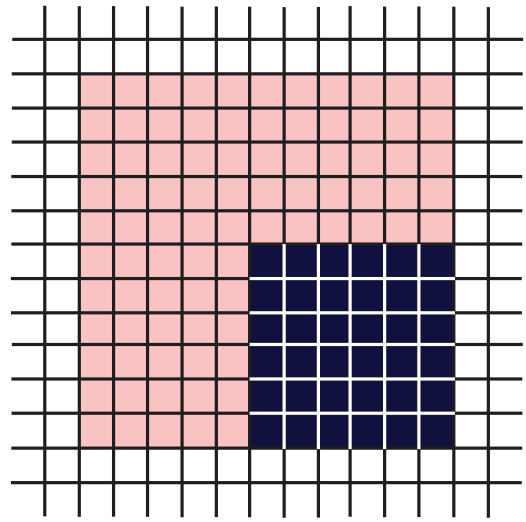

FIG. 1. (Color online) Assuming that the placement coordinate of the "square" ion is given by the position of its top-left corner, the dark-gray (blue) ion effectively occupies all the light-gray (pink) area as no ion of the same size can be put there. Note, however, that the volume excluded by the dark-gray (blue) ion would be smaller for other ions with a smaller size.

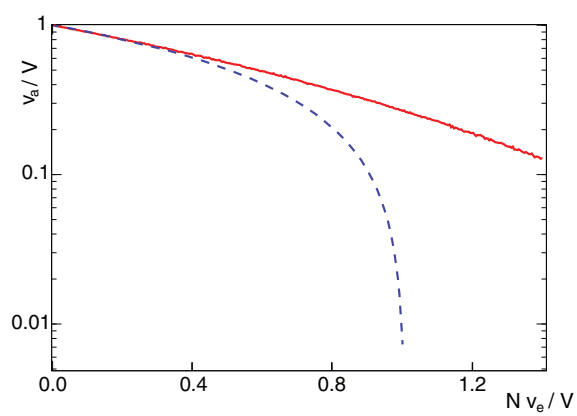

FIG. 2. (Color online) The volume available for insertion of an additional particle (v_a/V) in the box of volume V containing $N = cV$ particles, where c is the volume concentration of the particles in the box. The dashed (blue) line shows a prediction valid in the low-density regime, $v_a/V = 1 - cv_e$, where v_e is the volume each particle effectively excludes in the low-density regime. The solid line represents the results of Monte Carlo calculations performed with N hard spheres (top x axis), as explained in the text.

available for the insertion of an additional particle is given by $v_a/V = 1 - cv_e$, where c is the concentration and v_e is the volume a particle excludes in the low-density regime. This is represented with a dashed (blue) line in Fig. 2. The volume available for insertion was calculated numerically using Monte Carlo particle insertion techniques [26]. We performed such calculations for hard spheres of radii $r = l/2$ in a box of volume $V = 1000\,l^3$ with periodic boundary conditions, where l is an arbitrary unit of length. To each number of particles in a box N (the top x axis in Fig. 2), corresponds the concentration $c = N/V$. A volume available for insertion of the $(N+1)$th sphere was appropriately averaged over many initial configurations of N spheres [26], and the error of such a procedure is comparable with the thickness of the solid line in Fig. 2. For a hard sphere of radius r, the volume it effectively excludes in the low concentration limit is $v_e = 4\pi(2r)^3/3$, which was used as a scaling factor for the x axis in Fig. 2. One observes that the Monte Carlo simulations (solid line) agree with the simplest account of steric exclusion (line) in the low concentration limit, and start to significantly deviate when $cv_e > 0.4$ (since v_e is eight times the volume of the hard sphere, this would correspond to a packing fraction of 0.05).

We shall stay in the sufficiently low concentration limit, $c(L_{+,-}a)^3 \ll 1$, where the derivation we shall present can be most reliably applied. Now we write the expression for the number of configurations W. First we put in N_+ positive ions of the size L_+ and then N_- negative ones of the size L_- in the lattice, so that

$$\begin{aligned} W &= \frac{N\,[N-\Delta_+]\cdots[N-(N_+-1)\,\Delta_+]}{N_+!}\,\frac{[N-\Delta_\pm N_+]\cdots[N-N_+\Delta_\pm-(N_--1)\,\Delta_-]}{N_-!} \\ &= \Delta_+^{N_+}\Delta_-^{N_-}\binom{\frac{N}{\Delta_+}}{N_+}\binom{\frac{N}{\Delta_-}-\frac{\Delta_\pm}{\Delta_-}N_+}{N_-}, \end{aligned} \tag{2}$$

where $\Delta_{+,-} \equiv (2L_{+,-}-1)^3$ and $\Delta_\pm \equiv (L_+ + L_- - 1)^3$. In order to obtain the entropy density, $s = k_B \ln W$, where k_B is the Boltzmann constant, we expand the logarithms of factorials using Stirling's formula:

$$\begin{aligned} \frac{s}{k_B} &= -c_+\ln c_+a^3 - c_-\ln c_-a^3 + c_+\ln(\Delta_+a^3) + c_-\ln(\Delta_-a^3) - \frac{1}{\Delta_+a^3}\ln\Delta_+a^3 - \left(\frac{1}{\Delta_+a^3}-c_+\right)\ln\left(\frac{1}{\Delta_+a^3}-c_+\right) \\ &\quad + \left(\frac{1}{\Delta_-a^3}-\frac{\Delta_\pm}{\Delta_-}c_+\right)\ln\left(\frac{1}{\Delta_-a^3}-\frac{\Delta_\pm}{\Delta_-}c_+\right) - \left(\frac{1}{\Delta_-a^3}-\frac{\Delta_\pm}{\Delta_-}c_+-c_-\right)\ln\left(\frac{1}{\Delta_-a^3}-\frac{\Delta_\pm}{\Delta_-}c_+-c_-\right). \end{aligned} \tag{3}$$

We immediately observe that this expression is not symmetric in $+$ and $-$. This should come as no surprise, since we constructed W by *first* placing the positive and *then* the negative ions. We can expect to have symmetric entropy in the regime of small concentrations when the presented, approximate description of spatial correlations is valid. Before considering this limit we can let $a \to 0$ while keeping $V_i \equiv (2L_i)^3a^3$ constant [for indices $i = +, -, \pm$, with $L_\pm = \frac{1}{2}(L_+ + L_-)$]. This yields

$$\begin{aligned} \lim_{a\to 0}\frac{s}{k_B} &= -c_+\ln c_+a^3 - c_-\ln c_-a^3 + c_+\ln(1-V_+c_+) + c_-\ln(1-V_\pm c_+ - V_-c_-) \\ &\quad - \frac{1}{V_+}\ln(1-V_+c_+) - \frac{1}{V_-}\ln\left(1-\frac{V_-c_-}{1-V_\pm c_+}\right) + \frac{V_\pm}{V_-}c_+\ln\left(1-\frac{V_-c_-}{1-V_\pm c_+}\right), \end{aligned} \tag{4}$$

where $V_\pm \equiv [\frac{1}{2}(V_+^{\frac{1}{3}} + V_-^{\frac{1}{3}})]^3$. The first two terms seem divergent when $a \to 0$ but the divergences are repaired by the chemical potential terms in the free energy. We now expand the logarithms in terms of c_iV_j, which are assumed to be small:

$$\frac{s}{k_B} = -c_+\ln c_+a^3 - c_-\ln c_-a^3 - \frac{1}{2}[V_+c_+^2 + V_-c_-^2 + 2V_\pm c_+c_-] + c_+ + c_-. \tag{5}$$

As expected, this expression is now symmetric. Note here that we effectively obtain the contributions of the short-range (steric) repulsion in the free energy, proportional to c_+^2, c_-^2, and c_+c_-, similar to terms used by Kornyshev [8] to semiempirically extend the PB free energy functional. In that respect, we also note that $V_\pm$ is always positive [8]. We can now proceed to vary the free energy over concentrations, so as to obtain the Euler-Lagrange equations. The concentrations c_+ and c_- are then obtained by exponentiation, which yields exponential functions of c_iV_j—these are expanded to first order in c_iV_j to finally yield the modified PB equation. For a symmetric $z:z$ electrolyte, we obtain

$$\nabla^2\psi = \frac{2ezc_b}{\epsilon}\,\frac{\sinh\beta ez\psi + \frac{1}{2}c_b\,[(V_+ + V_- + 2V_\pm)\sinh\beta ez\psi - (V_+ - V_-)(\cosh\beta ez\psi - 1)]}{1 + c_b\,[(V_+ + V_-)\cosh\beta ez\psi + (V_- - V_+)\sinh\beta ez\psi] + c_b^2(V_+V_- - V_\pm^2)}. \tag{6}$$

We obtain the same modification of the standard PB equation as Borukhov *et al.* do [12] in the case when the ions have the same sizes, $V_+ = V_-$, and when c_jV_j are sufficiently small. It is intriguing that our approach predicts, as previous theories also do (e.g., Ref. [12]), the saturation of the ionic concentration in qualitative agreement with the maximal packing fraction.

It is of interest to examine the modification of the linearized PB equation, i.e., the dependence of the Debye-Hückel (DH) screening length λ on the ionic sizes. This is information we can easily get from our approach by linearizing Eq. (6) for small $e\beta\Psi$,

$$\lambda = \sqrt{\frac{kT\epsilon}{2e^2z^2c_b}\left[1 + c_b\left(\frac{V_+ + V_-}{2} - V_\pm\right)\right]}. \tag{7}$$

Since $V_+ + V_- \geqslant 2V_\pm$, the Debye-Hückel screening length is increased when ions are not of the same size (note again here that $c_jV_j \ll 1$), i.e., the effect of counterionic asymmetry persists in the lowest order in c_bV.

III. NUMERICAL EVALUATION OF THE MODIFIED PB EQUATION

A particular way to represent the effects of the asymmetry of screening ions, which can be used to relate the theoretical predictions to experiments, and which has been thoroughly discussed and analyzed by Kornyshev [8,24], is to calculate the double-layer differential capacitance C as a function of the plate potential U measured with respect to its bulk value. This is obtained as [24]

$$C = \left[\frac{dU}{d\sigma}\right]^{-1}. \tag{8}$$

Once the surface charge density is specified, the plate potential difference U can be calculated by solving Eq. (6)—this yields a $\sigma(U)$ dependence shown in Fig. 3, whose first derivative yields the double-layer capacitance shown also in Fig. 3.

We obtain the so-called "camel" profile of the capacity discussed in Ref. [8]. As explained by Kornyshev, the two-humped profile is a consequence of the finite volume of the screening ions. The double-layer capacity curve becomes asymmetric when $V_+ \neq V_-$. A similar dependence of σ and C on U has been obtained in numerical simulations of room temperature ionic liquids [24], and also in experimental studies of aqueous electrolytes [25]. Here we find the same effect and thus confirm the heuristic prediction put forth in Ref. [8]. Note, however, that the effect becomes prominent for quite large surface charge densities ($\sim$2 e/nm^2; note also that this depends on the bulk concentration c_0, which is 10 mM in the calculations presented), when the values of the plate potential are such that the DH linearization is completely inapplicable, $e\beta U \gg 1$. The effect can also be observed at smaller surface charge densities if the effective ionic volumes are sufficiently large, i.e., when the ions are poorly screening the plate charge. Our results can be directly compared with those obtained in Ref. [19], in particular, with Fig. 5 of that reference. We note that the positions of the maxima in a differential capacity nicely agree, and we have found that this agreement persists for different cationic sizes and salt concentrations. The magnitude of the differential capacity maximum is, however, about twice larger in our approach. This is not surprising in view of Fig. 2, and is a consequence of a too early onset of saturation of counterionic density that our approach predicts, similar as in Ref. [12], obtained for a sterically symmetric polyelectrolyte.

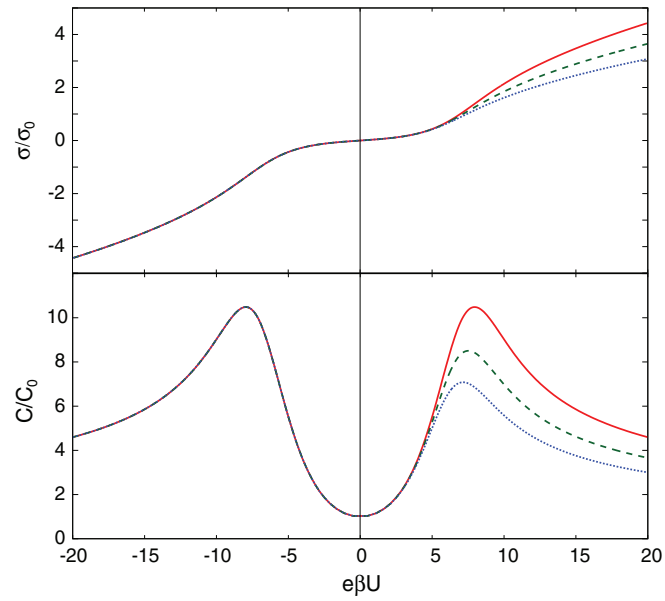

FIG. 3. (Color online) Top panel: The plate surface charge density σ as a function of plate potential difference U, $\sigma_0 = 1\ e/\text{nm}^2$. Bottom panel: The double-layer differential capacitance; $C_0 = e\sqrt{2\epsilon\beta c_0}$. The relative dielectric permittivity is $\epsilon_r = 80$, the monovalent bulk salt concentration is $c_0 = 10$ mM, the effective volume of the cation is $V_+ = 0.1505\ \text{nm}^3$ (cationic radius 3.3 Å), and the results for different anion volumes are indicated by solid ($V_- = V_+$; anionic radius 3.3 Å), dashed ($V_- = 1.53V_+$; radius 3.8 Å), and dotted ($V_- = 2.21V_+$; radius 4.3 Å) lines.

IV. CONCLUSIONS

We have presented the modification of the Poisson-Boltzmann equation based on a lattice-gas evaluation of the ionic entropy which allowed us to study the sterically asymmetric electrolytes. The particular derivation we presented shows several drawbacks of the simplest lattice-gas based counting schemes, as they fail to quantitatively and consistently account for the steric hindrance in the high-density regime of ionic concentrations. In particular, our work shows that the steric modification of the PB equation, including effects of ionic asymmetry, can be consistently performed in the regime of low ionic densities. Some previous steric modifications of the PB approach [12,21] assume independence of the occupation of neighboring cells. In this way, the difficulties in connecting the low- and high-density regimes are apparently avoided, as the "excluded volume" does not change in passing between the two regimes. We do note, however, that the problem we identify persists in these approaches also. Although our modification does predict the saturation of the ionic density in the high-density regime, the excluded volume parameter, i.e., effective ionic size, is to be treated with caution, as the physical content of this parameter is fixed in the low-density regime, where the spatial ionic correlations induced by steric hindrance can be easily described along the lines we presented.

The numerical evaluation of the modified PB equation shows the differences in screening efficiencies of cations and

anions, resulting in a characteristic asymmetric "camel" shape of the double-layer capacitance. The analytical framework we present provides also the basis for the heuristic approaches and modifications of the PB equation proposed previously in the literature [8].

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