A simple technique is proposed for numerically determining equilibrium ion distribution functions belonging to free energies of the Poisson-Boltzmann type. The central idea is to perform a conventional Monte-Carlo simulation using the free energy as the “Hamiltonian” entering the Metropolis criterion and the spatially discretized density as degrees of freedom. This approach is complementary to the possibility of numerically solving the differential equations corresponding to the variational problem, but it is much easier to implement and to generalize. Its utility is demonstrated in two examples: valence mixtures and hard core interactions of ions surrounding a charged rod.

I. INTRODUCTION

Understanding the interaction between charged macroions in solution requires knowledge of how the ions from the surrounding electrolyte screen the macroionic charge. A common starting point for the description of such systems is a mean field theory, which expresses the free energy as a functional of the ionic density. Accounting only for the electrostatic energy and the entropy of this density field yields (after functional minimization) the nonlinear Poisson-Boltzmann (PB) equation, which can be solved exactly in certain special cases. Since this approach neglects statistical correlations as well as the finite size of the small ions, various methods have been suggested which approximately account for those phenomena by adding correction terms to the free energy functional. However, the analytical treatment of those extended Poisson-Boltzmann theories is even harder than that of the original one; consequently, the desired ionic density profile is computed by numerically solving the complicated differential- or even integro-differential equations.

In this paper a method is proposed for determining the equilibrium ion distribution, which completely avoids differential equations. The key idea is to perform a straightforward Monte-Carlo (MC) simulation of the free energy functional. Although this is a numerical approach as well, it has the big advantage that its computational effort is mostly unaffected by the mathematical complexity of the functional under investigation. Only recently similar techniques have successfully been applied to the Onsager free energy functional from liquid-crystal theory.

II. DESCRIPTION OF THE MONTE-CARLO METHOD

This section briefly outlines the physical and mathematical background and proceeds with describing the Monte-Carlo scheme. For the sake of concreteness the derivations are presented within the framework of the cylindrical cell model, which is a commonly used approach for reducing the complicated many body problem of a solution of stiff polyelectrolytes (like, e.g., DNA) to an effective one polyelectrolyte theory. Upon (i) assuming that the surface of zero electric field surrounding one such molecule is on average a cylinder and (ii) neglecting edge effects by taking the length of the molecule to be infinite, one arrives at the geometry depicted in Fig. 1. A convenient measure for electrostatic interaction strength is the Bjerrum length \( \ell_B = \beta e^2 / 4\pi \varepsilon \) (\( k_B T = \beta^{-1} \) being the thermal energy and \( \varepsilon \) the dielectric constant), which permits the Coulomb energy for two unit charges \( e_0 \) a
distance \( d \) apart to be written as \( k_B T t_B / d \). Within a mean field density functional approach the counterions surrounding the rod are replaced by a cylindrically symmetric ion density \( n(r) \) (\( r \) is the radial coordinate) which gives rise to a likewise symmetric electrostatic potential \( \psi(r) \). The simplest ansatz for the free energy restricts to the electrostatic part of the energy and the entropy:

\[
F[n(r)] = L \int_{r_0}^{R} dr 2\pi r \left\{ \frac{\xi}{2} \left( \nabla \psi \right)^2 + \frac{n(r)}{\beta} \ln \frac{n(r)}{\bar{n}} \right\}.
\]

Here, \( \bar{n} \) is the average counterion density and \( L \) is the length of a cylinder subsegment, with respect to which all extensive quantities are to be measured in the following. Functional minimization of \( F \) under the constraint of global charge neutrality leads to the nonlinear Poisson-Boltzmann equation

\[
\Delta \psi(r) = \psi''(r) + \frac{1}{r} \psi'(r) = n(R) e^{\beta \epsilon_0 \psi(r)},
\]

which has to be solved subject to the boundary conditions

\[
\psi'(r_0) = -\frac{\lambda}{2\pi \varepsilon r_0}, \quad \psi'(R) = 0 \quad \text{and} \quad \psi(R) = 0.
\]

The analytical solution of (2,3) and in particular a discussion of the phenomenon of Manning condensation, which occurs for a charge parameter \( \xi = \lambda e t_B / e \rho \) larger than 1 can e.g. be found in Refs. This present paper suggests a method for (numerically) finding the distribution \( n(r) \) which minimizes functionals like (1) without using their corresponding differential equations.

Imagine the cell being subdivided by the \( M + 1 \) (not necessarily equidistant) splitting points \( s_0, s_1, \ldots, s_M \) (with \( s_0 = r_0 \) and \( s_M = R \)) into \( M \) concentric cylindrical shells of volume \( V_i = \pi (s_i^2 - s_{i-1}^2) L \). If furthermore the \( N_i \) ions within shell \( i \) are replaced by a density \( n_i = N_i / V_i \), the set \( \{N_i\} \) already completely specifies the (macro-)state of the system. The total electrostatic energy \( E \) of this configuration can be computed exactly by piecewise integration of the Poisson equation in cylindrical geometry, yielding

\[
E(\{N_i\}) = \frac{1}{4\pi \varepsilon} \sum_{i=1}^{M} \left\{ \left( Q_{i-1} - e_0 n_i \pi s_{i-1}^2 L \right) \ln \frac{s_i}{s_{i-1}} + e_0 N_i \left( Q_{i-1} + e_0 n_i \pi \frac{s_i^2 - 3s_{i-1}^2}{4} - 3s_{i-1}^2 L \right) \right\},
\]

where \( Q_{i-1} \) is the total charge up to but not including shell \( i \). The idea now is to perform a Markov process by randomly moving particles between the shells and accepting the moves with the usual Metropolis criterion. In the canonical ensemble the probability of a state \( \{N_i\} \) is proportional to the product of the Boltzmann factor

\[
P_E = \exp(-\beta E)
\]

and the probability \( P_S \) of distributing the (indistinguishable) ions between the shells in a way compatible with the given state, i.e.,

\[
P_S(\{N_i\}) = \frac{N!}{V^N} \prod_{i=1}^{M} \frac{V_i^{N_i}}{N_i!}
\]

where \( N = \sum_i N_i \) and \( V = \sum_i V_i \). Generate a new state \( \{N_i'\} \) from the old one by moving one ion from shell \( k \) to shell \( l \). Since

\[
\frac{P_S(\{N_i'\})}{P_S(\{N_i\})} = \frac{N_k}{V_k} \frac{V_l}{N_l + 1} = \frac{n_i^{\text{old}}}{n_i^{\text{new}}},
\]

detailed balance between the total probabilities finally yields the following acceptance probability of such a move:

\[
\text{Prob}(k \xrightarrow{1} l) = \min \left\{ 1, \frac{n_k^{\text{old}}}{n_l^{\text{new}}} e^{-\beta (E^{\text{new}} - E^{\text{old}})} \right\}
\]

There is an alternative way of looking at this: Since the entropy of a state is given by \( S = k_B \ln P_S \), the expression entering in (7) can actually be written as \( \exp(-\beta F) \), i.e., the “combinatoric” multiplicity of the states is automatically taken into account if the Metropolis criterion is tested with the free energy. Furthermore, if all \( N_i \) are large, the factorials in (6) can be approximated by Stirling’s formula:

\[
S(\{N_i\}) \approx -k_B V \sum_{i=0}^{M} n_i \ln \frac{n_i}{\bar{n}}.
\]

This is the shell-discretized equivalent of the entropy contribution entering into (1). By performing this Markov process one can thus sample the ion distribution function corresponding to the free energy functional (3) (after an initial equilibration time).

Some final remarks:

1. The proposed technique is applicable to all geometries in which the electrostatic energy can be computed efficiently once the charge density in the volume elements is known. In particular, this applies to the spherical and cylindrical cell model as well as the charged plane, because their high symmetry permits equations like (3).

2. Still referring to particles within a density functional theory might seem artificial: one could equally well transfer small bits of the density between shells (under conservation of the integral) and employ \( \exp(-\beta F) \) in the Metropolis criterion with the entropy contribution calculated from (7). However, Stirling’s approximation is only good for large \( N_i \), therefore, the global extensive prefactor in the exponential function must be large enough – for otherwise one even fails to reproduce a constant density in the limit of zero charge. Since in
the spherical geometry the size of this prefactor is not at one’s disposition (the total number of counterions per colloid is proportional to its finite and possibly small charge), equation (3) is to be preferred to equation (5).

3. Upon measuring the electrostatic interactions via the Bjerrum length, the explicit temperature dependence drops out of the Metropolis criterion.

4. Further contributions $F'$ to the free energy functional (e.g., excluded volume or correlation corrections) can be included by adding corresponding terms $-\beta \Delta F'$ in the exponential function of (5).

5. The approach bears some resemblance with the method of finite elements, for which the transformation from a differential equation to a functional minimization problem is a central idea.

III. EXEMPLARY APPLICATIONS

In order to demonstrate the utility of the described technique, this section presents two possible applications: Within the cell model described above the ionic distribution functions are computed for (i) a system with ions having different valences and (ii) a system with additional hard core interactions.

A. Valence mixtures

The PB equation in the cylindrical cell model cannot be solved analytically for a system containing a mixture of ions having different valences. For the MC approach, however, this is no problem, since it extends in an obvious way to such a situation: Each species of valence $v_j$ is represented by its own density $n_j(r)$ and a corresponding histogram. MC moves only act within the same histogram and the electrostatic energy is computed from the total charge density $\rho(r) = e_0 \sum_j v_j n_j(r)$. Figure 2 shows successive stages of an ion exchange process: The fraction of charge within a distance $r$ from the rod axis,

$$P(r) = \frac{1}{\lambda} \int_{r_0}^{r} d\bar{r} \, 2\pi \bar{r} \rho(\bar{r}), \quad (9)$$

is plotted for a system with $R/r_0 = 100$, $\lambda = \frac{1}{3} e_0/r_0$ and $\ell_B/r_0 = 1$, in which the neutralizing monovalent counterions are gradually (i.e., in steps of 10% of the charge) replaced by trivalent ones – until 100% of the charge is carried by the latter. The cell was subdivided into 500 shells with boundaries equidistant in $\ln r$, $10^6$ MC moves were performed to equilibrate the system and on average $5 \times 10^7$ further moves were used for sampling the distribution. The number of particles which were in minority ranged between 200 and 700.

As expected, the condensed fraction gets larger with increasing fraction of trivalent ions, i.e., the distribution functions are shifted upwards. Interestingly though, there is also a more subtle effect connected with the screening of the rod: It has recently been shown that within PB theory the point of inflection in $P(r)$ as a function of $\ln(r)$ localizes the condensation radius and the corresponding condensed fraction. If only one species of counterions is present, the locus of inflection points in $P(r)$ (parameterized by $\xi$) is solely determined by the cell geometry. In Fig. 2 it can be seen that for the mixtures the actual inflection points are shifted towards smaller radii, i.e., the rod charge is screened more efficiently. This effect must be attributed to global rearrangements of the counterions; the distribution of one species clearly depends on the distribution of the other, different valences are correlated – even on the PB level. A more detailed analysis in fact reveals that highvalent ions will gather in

FIG. 2. Poisson-Boltzmann charge fractions $P(r)$ (solid lines) from equation (5) for a valence mixture system with $R/r_0 = 100$, $\lambda = \frac{1}{3} e_0/r_0$ and $\ell_B/r_0 = 1$. The lowest curve corresponds to 100% monovalent counterions, while for the uppermost curve all ions are trivalent. From bottom to top the monovalent ions are gradually replaced by trivalent ones in steps of 10% of the charge. The dashed line indicates the locus of inflection points in $P(r)$ as a function of $\ln(r)$ for the PB theory with only one species of ions (in this case for varying $\xi$), whereas the heavy dots mark the actual inflection points in the distribution functions.
the vicinity of the rod at the expense of lowvalent ones. This provides a way of further decreasing the free energy, therefore, mixtures can screen more efficiently (i.e., within shorter distances) than solutions of only one valence. Notice finally that the observed shift implies that there is no “effective” valence \( v_{\text{eff}} \) such that a fictitious solution of counterions with valence \( v_{\text{eff}} \) gives the same distribution function as the actual valence mixture.

### B. Excluded volume

The free energy functional (1) of the plain Poisson-Boltzmann equation assumes no interaction beyond electrostatics. In particular, it neglects all effects resulting from an ionic hard core, which range from a suppression of high densities up to a packing of particles. A simple way for incorporating at least the density limitation is the free-volume approximation, characterized by the following contribution to the free energy density:

\[
\beta f_{\text{FV}}(n) = -n \ln \left(1 - n/n_{\max}\right),
\]

where \( n_{\max} \) is the maximally allowed density. (A related approach has recently been used to incorporate steric repulsion in the PB equation, see Ref.4.) After including (3) into (1), an MC simulation for a cell model has been performed with \( R/r_0 = 100, \lambda = 2\epsilon_0/r_0, \ell_B/r_0 = 1 \) and \( v = 3 \). As the limiting density \( n_{\max} = 3/2\pi d^3 \) has been chosen (with \( d/r_0 \in \{0, 1, \ldots, 10\} \)), which reproduces the correct second virial coefficient for hard spheres of diameter \( d \). 500 shells and 2000 particles have been used for \( d = r_0 \), while for systems with larger ions the number of shells has been reduced and the number of particles increased (50 shells and 50000 particles for \( d = 10r_0 \)) in order to avoid discretization effects occurring in the small innermost shells. After 200–500 MC steps per particle for equilibration, a further 5000–10 000 per particle have been used to sample the distributions. The effects on \( P(r) \) are shown in Fig. 3.

The distribution function for \( d = r_0 \) deviates only slightly from the one with \( d = 0 \). The reason for this is that the contact density in the absence of a hard core, \( n(r_0) = 0.447 r_0^{-3} \), is of the same order as the maximum density \( n_{\max,d=r_0} = 0.477 r_0^{-3} \). However, larger values of \( d \) bring about the expected changes: the contact density is reduced in the vicinity of the rod since the ions are pushed outwards. Therefore the sharp initial rise of \( P(r) \) shifts to larger values of \( r \) and softens out. Surprisingly though, the amount of condensation (for \( d = 0 \) one expects \( 1 - 1/\xi v \approx 83\% \)) is mostly unaffected by the pronounced changes in the ion distribution at small \( r \).

This can be seen from the straight line fit to the locus of relevant inflection points: Although the condensed layer considerably increases in size (from 14.3 \( r_0 \) up to 52.1 \( r_0 \)), the thus quantified condensed fraction decreases by less than one percent.

### IV. CONCLUSIONS

A method for finding the equilibrium ion distribution belonging to a free energy functional of the Poisson-Boltzmann type has been proposed. It avoids any reference to the differential equation corresponding to the variational problem, which makes it very easy to adapt to new free energy functionals. Its utility has been demonstrated in two examples, but its range of applicability is clearly much larger: It can also be used in the presence of salt, with additional free energy contributions (like, e.g., correlation corrections4) and in different geometries. In fact, the basic idea could be useful in the general context of functional minimization.
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