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Grand-canonical Monte Carlo method for Donnan equilibria

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We present a method that enables the direct simulation of Donnan equilibria. The method is based on a grand-canonical Monte Carlo scheme that properly accounts for the unequal partitioning of small ions on the two sides of a semipermeable membrane, and can be used to determine the Donnan electrochemical potential, osmotic pressure, and other system properties. Positive and negative ions are considered separately in the grand-canonical moves. This violates instantaneous charge neutrality, which is usually considered a prerequisite for simulations using the Ewald sum to compute the long-range charge-charge interactions. In this work, we show that if the system is neutral only in an average sense, it is still possible to get reliable results in grand-canonical simulations of electrolytes performed with Ewald summation of electrostatic interactions. We compare our Donnan method with a theory that accounts for differential partitioning of the salt, and find excellent agreement for the electrochemical potential, the osmotic pressure, and the salt concentrations on the two sides. We also compare our method with experimental results for a system of charged colloids confined by a semipermeable membrane and to a constant-NVT simulation method, which does not account for salt partitioning. Our results for the Donnan potential are much closer to the experimental results than the constant-NVT method, highlighting the important effect of salt partitioning on the Donnan potential.

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I. INTRODUCTION

Donnan equilibria are established in systems with partitions that selectively permit passage of some ionic species. For example, we can consider a system of charged colloidal particles separated from a salt solution by a semipermeable membrane with pores smaller than the colloidal diameter, but larger than the size of small ions or water. This leads to an unequal distribution of the small, permeable ions across the membrane, which induces a macroscopic electric potential across the membrane called the Donnan potential [1].

Donnan equilibria are important for a variety of technological and biophysical applications, including water purification [2,3], understanding DNA and polyelectrolyte brushes [4], and energy storage in batteries. It is also commonly encountered in biological systems where ion concentration gradients are maintained across semipermeable membranes. Because of this, the Donnan effect has been the subject of numerous theoretical [5–8] and simulation [9–14] studies aimed at predicting properties such as the electrochemical potential and osmotic pressure across the membrane.

Despite its importance, no existing simulation method properly accounts for the small ions partitioning unequally between the two sides of the membrane in an open system. In order to account for the selectivities of the different ions on either side of the membrane, they must be considered independently when performing grand-canonical moves. This violates charge neutrality, which is a requirement for the electrostatic energy to converge when using the Ewald sum [15]. Despite this, reliable results have been obtained in the past for systems that are charge neutral only in an average sense, as has been shown in Gibbs ensemble Monte Carlo studies of phase equilibria in ionic systems [16]. In confined systems, convergence is not a problem and the Donnan effect has been investigated in systems of small pores for which different concentrations of salt on either side of the membrane were observed [9–12]. We believe properly accounting for the unequal distribution of salt is vital for determining the correct Donnan potential, colloidal interactions, and other thermodynamic properties of the system.

A simulation-based approach for Donnan equilibria is highly desirable, as solution nonidealities and specific ion effects can then be fully taken into account. To this end, we outline a simulation method to study a system of charged particles confined by a semipermeable membrane that treats the salt ions grand-canonically. We compare our results to a theoretical approach, which also takes the grand-canonical nature of the problem into account. We also compare our method to experimental results for the Donnan potential in a system of charged colloidal particles, and in addition, compare this to a simulation method that does not treat the salt grand-canonically in order to highlight the importance of taking this into account.

II. SIMULATION METHOD

Our goal is to model a system with a semipermeable membrane that has large colloidal particles that cannot pass through, and small ions that can pass through. A schematic of this is shown in Fig. 1. For simplicity, we use the primitive model where colloids and ions are treated as charged hard spheres with diameter σ, in general different for each species, and charge q.

The Coulomb interaction between two particles with charge q_i and q_j, respectively, that are separated by a distance $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is given by

$$\beta V(r_{ij}) = \frac{\lambda_B q_i q_j}{r_{ij}}, \tag{1}$$

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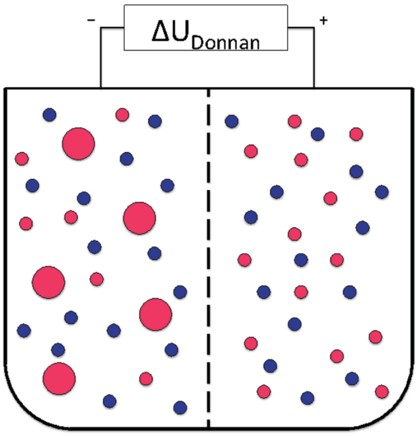

FIG. 1. (Color online) Schematic illustration of Donnan equilibrium. The large particles, each carrying a charge of −2, are not able pass through the membrane. The small ions, with charges −1 and +1 respectively, can pass freely between the two sides. A potential difference is established across the membrane.

where $\lambda_B = e^2/4\pi\varepsilon_0\varepsilon_r k_B T$ is the Bjerrum length, e is the elementary charge, ε_0 is the permittivity of free space, ε_r is the relative dielectric constant, k_B is Boltzmann's constant, T is the absolute temperature, and $\beta = 1/k_B T$. These interactions are calculated using the particle-particle–particle-mesh Ewald method of Hockney and Eastwood [17].

To account for the small ions passing through the membrane, we use a grand-canonical Monte Carlo (GCMC) scheme where the small ions are inserted or deleted independently of each other, however the colloidal particles are only moved locally, never inserted or deleted. By decoupling the positive and negative salt species, electroneutrality will be instantaneously violated during the simulation. However, as long as the system is on average charge neutral, the effect of this is negligible. We demonstrate this by simulating a two-component system and either insert and delete neutral groups or treat both particle types independently. In these simulations, the negative ion has a charge valence of $q_- = -1$ and hard-sphere diameter of $\sigma_- = 1.0$ nm. For the positive ion $q_+ = 2$ and $\sigma_+ = 3.0$ nm, and we set the Bjerrum length to $\lambda_B = 2.0$ nm. We compare the concentration of each ion for different chemical potentials of the positive and negative ions, μ_+ and μ_- respectively, in Table I. When the ions are treated independently, a number of simulations are performed to determine the values of μ_+ and μ_-, which result in an electroneutral system at a target concentration. Histogram reweighting [18,19] is used to accelerate this process. We then use these chemical potentials for the simulations of neutral groups, where we we adopt the approach of Valleau and Cohen [20] to combine the values of μ_+ and μ_- accordingly. The excellent agreement between the two simulation methods shows that electroneutrality does not need to be maintained for every configuration to get reliable results using Ewald-based methods. We note that we do not include the charged system term of the Ewald sum commonly used to study one-component plasmas [21],

$$U_{\text{charged}} = -\frac{1}{8\varepsilon_0 V\alpha^2}\left|\sum_{i=1}^{N} q_i\right|^2, \tag{2}$$

where V is the system volume and α controls the splitting of the energy between real space and Fourier space. This is the energy of the charged particles with a uniform neutralizing background charge. If this term were included, a grand-canonical move would compare the energies between two different systems, each with a different value for the uniform background charge. By excluding this term, the physical system does not change, however, the energy of non-neutral configurations diverges for periodic systems. Since the Ewald sum is truncated in both real and in Fourier space, we do not end up with infinite energies and the resulting error is negligible, as is evidenced by our results in Table I. It would be necessary to perform such tests to ensure this holds for future systems of interest. We believe this method, while not ideal, is nonetheless better than alternative methods for electrostatic interaction such as reaction-field [22], using the minimum image convention [23], or simple truncation or the Coulomb potential. Another more practical consideration is that U_{charged} favors a system with a net charge and including it results in an unstable simulation. Once a system obtains a net charge, Monte Carlo moves that increase that net charge are favored and this leads to the system being filled with only positive or only negative particles.

TABLE I. Chemical potentials, μ_+ and μ_- and the corresponding particles numbers N_+ and N_- for simulations where the ions are inserted or deleted either independently or as neutral groups.

		Neutral groups		Independent ions	
$\beta\mu_+$	$\beta\mu_-$	N_+	N_-	N_+	N_-
−7.139	−5.744	50.03(3)	100.1(1)	50.10(7)	100.2(1)
−6.398	−4.972	100.1(1)	200.3(1)	100.1(1)	200.3(2)
−5.240	−4.062	199.5(2)	399.1(3)	199.4(2)	399.1(4)
−2.453	−2.795	400.4(3)	800.9(7)	401.0(5)	801.3(8)

With this now established, we can proceed to devise a method to accurately determine properties of the Donnan system. We first perform a simulation with only salt ions, representing the reservoir salt concentration. Histogram reweighting [18,19] is used to determine the values of $\mu_{\text{bulk},+}$ and $\mu_{\text{bulk},-}$, which result in a system that is on average electroneutral and has the target salt concentration. A second simulation is then performed, which contains the colloidal particles at a fixed concentration. In general, using $\mu_{\text{bulk},+}$ and $\mu_{\text{bulk},-}$ will result in a system with a net charge. In order to satisfy the global electroneutrality condition, the chemical potentials must be shifted by a value $\beta q U_{\text{Donnan}}$, where U_{Donnan} is the Donnan potential, such that $\mu_+ = \mu_{\text{bulk},+} + \beta q_+ U_{\text{Donnan}}$ and $\mu_- = \mu_{\text{bulk},-} + \beta q_- U_{\text{Donnan}}$. In general, a number of simulations must be performed to find the value of U_{Donnan} that results in a neutral system and to accelerate this process we use histogram reweighting techniques [18,19]. In this way we have a simple, robust method to determine the Donnan potential using GCMC simulations of two separate systems, one with only salt at the target reservoir concentration, and one with the target colloid concentration. Because moving colloids in a system with much smaller particles is difficult, causing the colloids decorrelate slowly, we use the geometric cluster algorithm for charged systems. However, it has been shown that for these systems the colloid degrees of freedom have little impact on the Donnan potential [5].

III. RESULTS

The Donnan equilibrium method outlined in Sec. II allows us to perform simulations that overcome an important limitation of prior simulation studies of Donnan equilibria in open systems, namely the ability of the salt to partition unequally between both sides of the membrane. Our simulation method does correctly take this into account. In this section, we compare results from this approach to a theory that also treats the salt grand-canonically, and indeed predicts unequal salt partitioning [8].

In the system we use to compare our results with the theory, the colloidal particles have a hard-sphere diameter of 43.8 nm and charge of $Z = 50$, the reservoir salt concentration is 10^{-5} mol/l and $\lambda_B = 2.37$ nm, which corresponds to a solvent of ethanol at room temperature. We use monovalent salt; in the theory, the size of the ions is not taken into account. In the simulations however, we choose a hard-sphere diameter of 0.4 nm. To demonstrate the effect of salt partitioning, we determine both the total number of ions in the system and the amount of added salt. Following the convention in Ref. [8], the total ion concentration is $\rho_+ + \rho_-$ while the amount of added salt is $\rho_+ + \rho_- - Zn = 2\rho_-$, where n is the colloid concentration. In this way, the amount of added salt does not count the counterions coming from colloidal particles. The results for these quantities as the colloid concentration is increased are given in Fig. 2. Our results for the total ion concentration match very well with the theory, while the results for added salt show only a small quantitative difference at high η, which is likely due to the finite size of the ions in the simulations. We also compare our results for the Donnan potential and osmotic pressure, Π, and find excellent agreement as shown in Figs. 3 and 4.

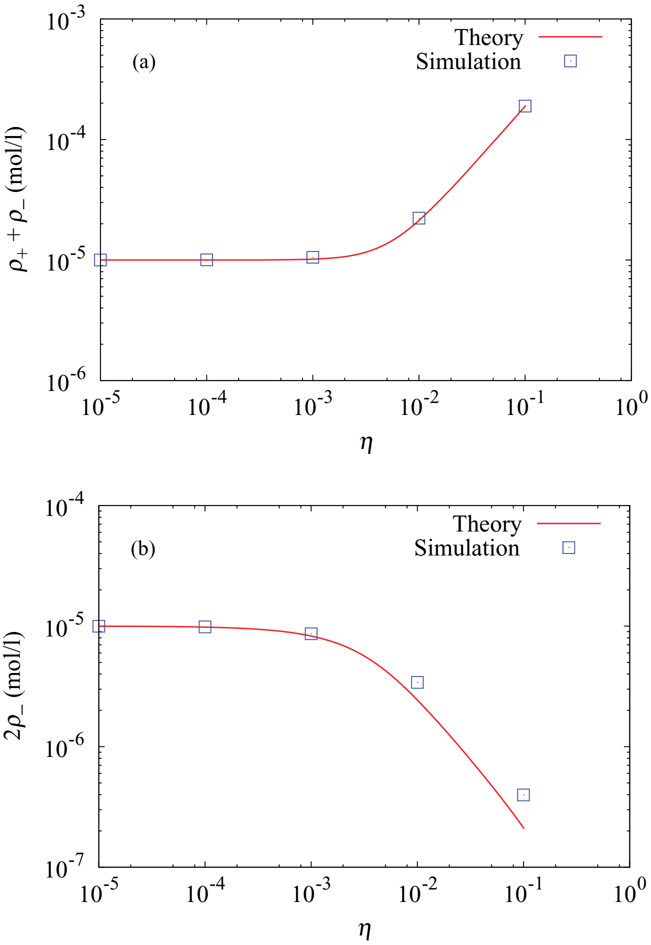

FIG. 2. (Color online) Total ion concentration (a) and added salt (b) as a function of colloid concentration. The red line is computed using Eqs. (25) and (27) of Ref. [8]. The error bars for the simulation results are smaller than the symbol size.

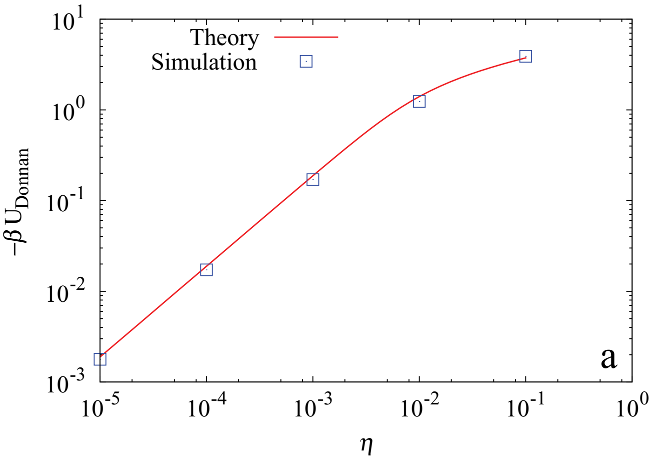

FIG. 3. (Color online) Donnan potential as a function of colloid concentration. The line is computed using the theory described in Ref. [8]. The error bars for the simulation results are smaller than the symbol size.

The Donnan potential calculations can also be directly compared to experimental results for a colloidal system with added salt [24]. Here λ_B as well as the charges and sizes of the colloids and ions are the same as before, however the semipermeable membrane separates one compartment with a colloid

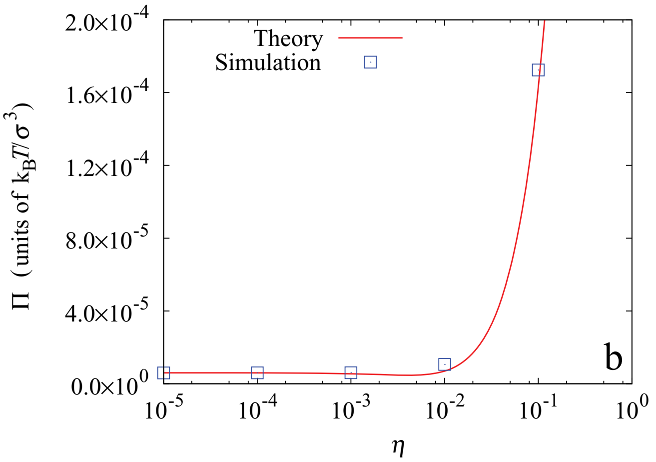

FIG. 4. (Color online) Osmotic pressure, Π, as a function of colloid concentration. The line is computed using the theory described in Ref. [8]. The error bars for the simulation results are smaller than the symbol size.

TABLE II. Chemical potentials, μ_+ and μ_- and the corresponding particle numbers N_+ and N_- for our method using GCMC and for constant-NVT simulations using the Widom insertion method [25] to determine the chemical potentials assuming the same salt concentration in each compartment.

	GCMC				Vlachy and Prausnitz [5]			
	$\beta\mu_+$	$\beta\mu_-$	N_+	N_-	$\beta\mu_+$	$\beta\mu_-$	N_+	N_-
Reservoir	−10.992	−10.992	662.8(8)	662.9(8)				
$\eta = 1.2 \times 10^{-3}$	−10.951	−11.032	695.2(9)	644.9(9)	−10.926(4)	−11.005(1)	712	662
$\eta = 1.3 \times 10^{-2}$	−10.592	−11.392	1033.9(9)	484.3(8)	−10.404(4)	−11.122(4)	1212	662

volume fraction of $\eta = 1.2 \times 10^{-3}$ and one compartment with a volume fraction of $\eta = 1.3 \times 10^{-2}$ and the reservoir salt concentration is 30×10^{-6} mol/l. To determine the Donnan equilibrium for this system, where there are colloids in both compartments, three systems need to be simulated. A system with no colloids is simulated to determine the values of $\mu_{\text{bulk},+}$ and $\mu_{\text{bulk},-}$, which yield the correct reservoir salt concentration. In addition, both colloid concentrations need to be simulated to find the corresponding values of U_{Donnan}, which yield a neutral system. The Donnan potential between the two compartments is then the difference between U_{Donnan} for the two systems. The chemical potentials and particle numbers for these three systems are given in Table II. The Donnan potential determined from our simulations is -9.22 ± 0.01 mV, while the experimental result is -12.9 ± 0.5 mV [24]. This is likely due to a limitation of the model as the theory of Zoetekouw and Roij [8] predicts a value of −9 mV for the same system.

We demonstrate the importance of considering the salt grand-canonically by comparing our results to those obtained assuming that the salt concentration is identical on both sides of the semipermeable membrane as done in the work of Vlachy and Prausnitz [5]. Using the method of Ref. [5], one simply performs a constant-NVT simulation for the two colloid concentrations and determines the chemical potentials for the positive and negative ions in each system using the Widom insertion method [25]. As before, the counterions that neutralize the colloidal particles are not included in the salt concentration hence different values for N_+ while N_- remains constant in Table II. We do this for the experimental system described above and find a Donnan potential of -3.00 ± 0.01 mV, which is much lower than either our method or the experiments. The chemical potentials from the two methods are given in Table II and we can see that the ion concentrations are also quite different when they are treated grand-canonically. When the salt concentration in each compartment is assumed to be the same, there is no guarantee that the systems will be in electrochemical equilibrium with each other. Using our proposed grand-canonical scheme solves this problem. Interestingly, in the experimental system, when salt bridges were used to maintain an equal amount of salt on both sides of the membrane, a Donnan potential of −3.00 mV was measured [24].

IV. CONCLUSION

In this work, we have presented a simulation approach to study a system of charged particles confined by a semipermeable membrane. A key aspect of this method is using a single ion instead of neutral ion groups for the grand-canonical moves. This decouples the positive and negative ions and allows for different ionic concentrations on either side of the membrane. The method was validated by comparing the results to theoretical calculations that take into account the different ionic concentrations on either side of the membrane. Donnan potentials from experimental measurements were also found to be in excellent agreement with the simulation results.

While we have focused on colloidal systems to demonstrate this method, it can be easily applied to a variety of other systems including polymers and biological systems: for example, proteins confined by a semipermeable membrane. These systems generally include specific interaction with the salt ions or ion correlations close to the impermeable particle, which are difficult to account for using theoretical approaches. These effects are usually easy to include in simulations, however. One potential drawback of our method is that grand-canonical moves pose a great challenge if the solvent is included explicitly. However, for many systems of interest, the solvent need not be modeled explicitly to get reliable results.

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