state energy eigenfunction of the inversion problem. Numerical solution of the approximate energy eigenvalue problem again has been made by infinite matrix diagonalization. For illustration we give below the lowest torsionality energy levels for CH$_3$NH$_2$ based on barrier values reported by Itoh$^{37,38}$ and Lide$^{39}$ for this work $V_z = 691.1$ cm$^{-1}$ has been chosen.

$\Gamma(0+)(g=1): 144, 600, 926, 1577, 2519$
$\Gamma(0-)(g=1): 414, 910, 1577, 2519$
$\Gamma(1)(g=2): 144, 408, 637, 773, 1105, 1325, 1860, 2174$

Supplementary Material Available: The complete Table II containing the 66 experimental points displayed in Figure 2 (1 page). Ordering information is given on any current masthead page.

References and Notes

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Ion Distributions in Lamellar Liquid Crystals. A Comparison between Results from Monte Carlo Simulations and Solutions of the Poisson–Boltzmann Equation

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Monte Carlo (MC) simulations have been performed for an ionic system between two parallel uniformly charged plates modeling the conditions found in lamellar lyotropic liquid crystals. The results are used to assess the accuracy of the statistical-mechanical approximations leading to the Poisson–Boltzmann (PB) equation. In general there is a good agreement between the MC simulations and the results obtained from the PB equation. This applies to the ion distribution and to a lesser extent to the energy. In particular the PB equation predicts the correct asymptotic behavior as the distance between the plates is increased. In the MC simulations there is a slight increase in the ion concentration close to the walls compared to the PB solution. This is due to the fact that in the MC simulations one allows for correlations between the ions, whereas the PB equation is derived under the assumption that the pair correlation function is constant. It is shown that the accumulation of ions close to the walls is solely due to the repulsions between the ions, and it is argued that ion binding in a polyelectrolyte system can be understood as caused by the incapability of the bulk solution to sustain a substantial net charge over moderately large distances.

Introduction

The physical-chemical properties of charged macromolecules and aggregates in an aqueous medium are strongly influenced by electrostatic effects. A large species having a high surface charge will attract counterions to reduce the electrostatic repulsions at the surface. When studying the ion binding in such systems, one either can be directly interested in the ion distribution as it is probed in a spectroscopic or kinetic experiment or can focus on the

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the attention on the energetic effects of the electrostatic interactions. These influence ion activities, osmotic pressures, macromolecule or aggregate conformations, phase equilibria, and interparticle forces.

The counterion distribution in polyelectrolyte systems has in recent years been thoroughly investigated, and a number of remarkable invariance properties have been found. The counterion binding is mainly determined by the surface charge density at the polyelectrolyte, and it is largely independent of salt concentration, polyelectrolyte concentration, and temperature. These properties, which are sometimes summarized as manifestations of an ion-condensation behavior, can be derived from the Poisson–Boltzmann equation, but alternative derivations also exist. There is in general a very good agreement between these predictions about the ion distribution and experimental investigations. For quantities related to energies, the agreement between theory and experiment is somewhat less satisfactory. For phase equilibria the Poisson–Boltzmann equation gives a remarkably good description, whereas for ion activities and osmotic pressures there is qualitative but not quantitative agreement.

In the present paper we aim at finding some of the reasons for the success of the simple theory based on the Poisson–Boltzmann (PB) equation. The problem is approached by formulating the statistical-mechanical approximations of the PB equation. We then study a model system consisting of two charged plates with an intervening solution containing only counterions by using the Monte Carlo (MC) simulation technique. This model system conforms closely to the conditions found in lyotropic lamellar liquid crystals.

Poisson–Boltzmann Equation for Inhomogeneous Systems

In a statistical-mechanical treatment of ions distributed in a medium of constant permittivity \( \varepsilon_{eo} \) the Poisson–Boltzmann equation

\[
-\varepsilon_{eo} \nabla^2 \Phi = \sum_{\alpha} Z_{\alpha} e \varepsilon_{eo} \exp(-Z_{\alpha} e \Phi / kT)
\]

is usually derived by assuming that the potential of mean force for an ionic species \( \alpha \) is \( Z_{\alpha} e \Phi \) where \( Z_{\alpha} \) is its valency, \( e \) the unit charge, and \( \Phi \) the mean electrostatic potential. However, to increase the physical insight and to obtain explicit expressions for the correction terms, we have re-derived eq 1 with special emphasis on inhomogeneous systems.

In an inhomogeneous system the one-particle distribution function \( n_\alpha(\mathbf{r}) \) describes the concentration variation of species \( \alpha \) relative to the fixed center. According to the first member of the Yvon hierarchy, for the equilibrium particle distribution functions one has

\[
-kT \nabla^2 \ln [n_\alpha(\mathbf{r})] = \sum_\beta \int \left( U_{\alpha\beta}(\mathbf{r},\mathbf{r'}) - \frac{a_\alpha(\mathbf{r})}{4\pi \varepsilon_{eo} |\mathbf{r} - \mathbf{r'}|} \right) n_\beta(\mathbf{r'}) d^3 r'
\]

where \( U_{\alpha\beta}(\mathbf{r},\mathbf{r'}) \) is the external potential for particles \( \alpha \) and \( \beta \), and \( a_\alpha(\mathbf{r}) \) is their two-particle distribution function. Equation 2 may be rewritten by expressing \( n_{ad} \) in terms of particle correlation functions

\[
\sum_\beta \int \left( U_{\alpha\beta}(\mathbf{r},\mathbf{r'}) - \frac{a_{\alpha\beta}(\mathbf{r},\mathbf{r'})}{4\pi \varepsilon_{eo} |\mathbf{r} - \mathbf{r'}|} \right) n_\beta(\mathbf{r'}) d^3 r' = \frac{Z_{\alpha} e}{4\pi \varepsilon_{eo} |\mathbf{r} - \mathbf{r'}|} \]

The right-hand side of eq 2 is now split into three terms

\[
-kT \nabla^2 \ln [n_\alpha(\mathbf{r})] = \sum_\beta \int \left( U_{\alpha\beta}(\mathbf{r},\mathbf{r'}) - \frac{a_{\alpha\beta}(\mathbf{r},\mathbf{r'})}{4\pi \varepsilon_{eo} |\mathbf{r} - \mathbf{r'}|} \right) n_\beta(\mathbf{r'}) d^3 r'
\]

where the first term is due to the external potential, the second term represents the average interaction of all particles with a particle of type \( \alpha \) at \( \mathbf{r} \), and the third term is the correction due to particle correlations. If the interaction is purely electrostatic and

\[
U_{ad}(\mathbf{r},\mathbf{r'}) = \frac{Z_{\alpha} Z_{\beta} e^2}{4\pi \varepsilon_{eo} |\mathbf{r} - \mathbf{r'}|}
\]

then the integral

\[
\sum_\beta \int U_{ad}(\mathbf{r},\mathbf{r'}) n_\beta(\mathbf{r'}) d^3 r' = Z_{\alpha} e^2 \Phi(\mathbf{r})
\]

where \( \Phi(\mathbf{r}) \) is the mean electrostatic potential due to the mobile ions in the system. If the third term in the right-hand side of eq 4 is neglected, i.e., if \( g_{ad}(\mathbf{r},\mathbf{r'}) = 1 \), the equation can be integrated directly to give

\[
n_\alpha(\mathbf{r}) = n_{0\alpha} \exp\left(-Z_{\alpha} e \Phi(\mathbf{r}) / kT\right)
\]

If furthermore one adopts the primitive model for \( U_{ad}(\mathbf{r},\mathbf{r'}) \) so that \( U_{ad}(\mathbf{r},\mathbf{r'}) = Z_{\alpha} e \Phi(\mathbf{r}) \) for \( \mathbf{r} \) within the volume \( V \), \( U_{ad}(\mathbf{r},\mathbf{r'}) = 0 \), otherwise

\[
n_\alpha(\mathbf{r}) = n_{0\alpha} \exp\left(-Z_{\alpha} e \Phi(\mathbf{r}) / kT\right)
\]

where the total electrostatic potential \( \Phi = \Phi_\Phi + \Phi_i \) is the sum of the external, \( \Phi_\Phi \), and internal, \( \Phi_i \), potentials.

The PB equation can now be derived by taking the divergence of eq 4 and setting \( h_{ad} = 0 \). Then

\[
kT \nabla^2 \ln [n_\alpha(\mathbf{r})] = \sum_\beta \int Z_{\alpha} Z_{\beta} e^2 \frac{n_\beta(\mathbf{r})}{4\pi \varepsilon_{eo} |\mathbf{r}|^2}
\]

Insertion of eq 8 into eq 9 gives the Poisson–Boltzmann equation, within the volume \( V \). The approximations leading to the PB equation can be summarized as the following:

(i) The interaction between the mobile ions in the solution is of a pure Coulomb type as in eq 5.

(ii) The pair correlation function \( g_{ad} \) between the mobile ions is constant and unitary.

(iii) The interaction between the mobile ions and the fixed center follows the primitive model with an electro-
static term and a hard wall cutoff.

One can note that for a system containing both negative and positive mobile ions the assumptions i and ii are interconnected so that if the ion correlations are treated exactly one must introduce an additional repulsive term in the interaction potential to prevent the ions from merging.

In evaluating the effects of neglecting the last term in eq 4, one can use analytical approximations to $h_{ab}$ preferably in terms of the direct correlation function. This has recently been done by Fixman28 using an equation similar in structure to eq 4 and by Henderson and co-workers29,30 starting from the Ornstein-Zernike equation for a binary mixture. An alternative approach, which we have adopted, is to solve the statistical-mechanical problem through a Monte Carlo simulation. Recently Torrie and Valleau31 presented such a study for a single charged wall in contact with an electrolyte solution and compared the resulting ion distribution with that found by solving the PB equation.

Lyotropic Lamellar Liquid Crystals

When experimentally studying the molecular interactions in the interfaceal region between an aqueous medium and a region of lower polarity, one is often faced with the problem that the specific effects due to the interface are masked by the behavior in the bulk solution. One type of system where this problem can be largely overcome is lyotropic liquid crystals, which are formed from mixtures of amphiphilic (surface active) molecules and water.25 In these systems the interfaceal region accounts for a large fraction of the total sample volume. They are thermodynamically stable and can be characterized geometrically through low-angle X-ray scattering. Furthermore the macroscopic anisotropy makes it possible to study orientation effects.

From a theoretical point of view these systems are attractive since symmetry arguments can be used to simplify calculations considerably. The commonly studied lamellar systems, in particular, possess on the average a cylindrical symmetry. The structure of such a lamellar system formed by an ionic amphiphile is schematically illustrated in Figure 1. The amphiphilic forms apolar bilayers which are intercalated with aqueous sheets containing the counterions. The aqueous region also contains some dissolved amphiphiles, but often to a negligible extent.

When considering the electrostatic interactions in such a system, one can first note the peculiar fact that, if the charge on the bilayer surface is considered as uniformly distributed, the electrostatic potential, $\Phi_{\text{ion}}$ from the two surfaces is constant in the intervening solution. Then the nonuniform distribution of the ions is determined entirely by the hard-wall potential and the interactions between the mobile ions themselves, being independent of the charge density of the walls. This is, in our opinion, an important observation, and it provides a clue to a conceptual understanding of ion binding in polyelectrolyte systems. It also shows that the approach used by Fixman28 to discuss the electrostatic effects is inapplicable in the present case, for which the key equation 2.16 of ref 28 is of the character $0 = 0$. A further consequence of the geometry is that image charge effects are absent on the average so that they do not appear within the PB approximation.

For the system of Figure 1 the solution of the PB equation gives

$$\Phi(Z) - \Phi(0) = \frac{(2kT/Ze) \ln(\cos(sz/b))}{(s^2z/b+2)}$$

$$\rho(z) = \frac{(e_{\text{eq}}, 2kT \sigma^2/Ze b^2)}{\cos^2(sz/b)}$$

where $\rho(z)$ is the charge density. The dimensionless parameter $\sigma$ characterizing the solution is determined through the boundary condition

$$s \tan(s) = K = -2 \sigma e b / (2 \sigma e k T)$$

where $\sigma$ is the surface charge density on the plates for an electrolyte system. If one allows for both negative and positive ions in the aqueous medium, the solution to the PB equation becomes more complex, involving elliptic integrals.8,14

From these two sets of solutions it was shown that the ion distribution behaves according to the simple rules summarized in the "ion condensation" model described in the introduction. A comparison with experimental studies of the ion distribution using NMR corroborate the conclusions concerning these qualitative rules.17 It is clear that the "ion condensation" behavior is caused by the long-range ion-ion interactions, and it is qualitatively different from the behavior of systems where only short-range forces are involved. It is then a challenge to try to understand the particular behavior in a more rigorous statistical-mechanical framework.

Monte Carlo Simulations

The Monte Carlo simulations were performed by using the well-known technique of Metropolis et al.32,33 where the statistical average

$$\langle f \rangle = \frac{\int f(X) \exp(-U(X)/kT) dX}{\int \exp(-U(X)/kT) dX}$$

is approximated by a finite number of points in the configuration space

$$\langle f \rangle \approx 1/M \sum_{|X|} f(X)$$

and the configurations $X_i$ are sample weighted by the Boltzmann factor $\exp(-U(X)/kT)$. The symbols $M$ and $U(X)$ are the number of configurations and the interaction energy of the $N$ particle in the studied system, respectively. The number of particles in the systems studied ranges from 2 to 200, and it was found that ~2000 configurations/particle was sufficient to obtain a statistical error of less than one percent in the energy average $\langle U \rangle$, provided a similar number of configurations had been generated to equilibrate the system. The statistical errors were estimated by the aid of subaverages according to Wood.53 It was found by test calculations that an optimal value for the maximum step size in the realization of the Markov chain was 3–6 Å. The simulations were performed in the canonical ensemble at a temperature of 301 K. The "Monte Carlo box" was a parallelepiped with the dimensions $2a \times 2a \times 2b$, where $2b$ is the distance between the two charged plates (see Figure 1) and $a$ is determined by $N$. The simulations were performed at a constant charge density on the plates of 1 unit charge per 71.4 Å$^2$, which is a typical value found in lamellar systems.25 Periodic boundary conditions were applied in the two directions ($x$ and $y$) parallel to the plates. Most of the computer time is spent in the evaluation of the ion-ion interaction, and this part of the program has been written directly in machine code using a special technique to evaluate the SQRT function. The CPU time for a simulation with 8 x $10^8$ configurations and 200 ions was ca. 2 h on a UNIVAC 1100/80 system.
In the simulations the energy of a given configuration was calculated by using a Coulomb ion–ion interaction as in eq 5 and an external potential \( U(z) \). In all simulations \( U(z) \) contains a hard-wall part so that \( U \rightarrow \infty \) when \( |z| > b \). To obtain insight into the long-range effects on the ion distribution and on the energy, simulations were performed with different external potentials \( \Phi_e \). In the limit of an infinite system, \( \Phi_e \) tends to a constant independent of \( z \). However, when the number of particles in the system is increased, the convergence with respect to the ion distribution is influenced by the choice of \( \Phi_e \).

The computationally simplest choice is to make \( \Phi_e = 0 \). The result of such a series of simulations is shown in Table 1. In this and the forthcoming tables we have chosen to characterize the ion distribution through three parameters: \( c_{\text{max}} \), the concentration of ions within a layer of 0.2 Å from the wall; \( S_1 \), the fraction of ions within a distance of 3 Å from the walls; and \( S_c \), the entropy, relative to an ideal gas. The concentrations \( c \) are calculated as averages over layers of thickness 0.1 Å. The data in Table I show that the energy diverges when \( N \) is increased as it should since the system is not electroneutral. Furthermore the convergence in the ion distribution is slow, and even at \( N = 200 \) one is still far from convergence, illustrating the long-range character of the ion–ion interaction.

The convergence is improved considerably when the system is made electroneutral with a compensating smeared-out charge on the walls although the calculations are still made within the minimum image (MI) convention. In this case the units for \( E, S, \) and \( c_{\text{max}} \) are kJ/mol, J/(mol K), and \( \text{mol} \), respectively. For the definition of the entropy \( (S_c) \), the maximum concentration \( (c_{\text{max}}) \), and the fraction bound ions \( (p_b) \), see the text. The statistical error in the simulated energy is \( \pm 0.2\% \) and in the other properties \( \pm 2\% \).

### Table I: Convergence of the MC Simulations with the External Potential \( \Phi_e = 0 \) and \( b = 10.5 \text{ Å} \)

<table>
<thead>
<tr>
<th>( N )</th>
<th>( E_{\text{II}} )</th>
<th>( E_{\text{TW}} )</th>
<th>( E_{\text{II} - \text{PB}} )</th>
<th>( E_{\text{II} - \text{PB}} )</th>
<th>( E_{\text{II} - \text{PB}} )</th>
</tr>
</thead>
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<tr>
<td>20</td>
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<td>17.35</td>
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</tr>
<tr>
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<td>31.75</td>
</tr>
<tr>
<td>60</td>
<td>23.15</td>
<td>21.25</td>
<td>26.90</td>
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<td>34.50</td>
</tr>
<tr>
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<td>29.80</td>
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<td>36.50</td>
</tr>
<tr>
<td>150</td>
<td>28.85</td>
<td>26.00</td>
<td>32.70</td>
<td>35.60</td>
<td>39.40</td>
</tr>
</tbody>
</table>

The units for \( E, S, \) and \( c_{\text{max}} \) are kJ/mol, J/(mol K), and \( \text{mol} \), respectively. For the definition of the entropy \( (S_c) \), the maximum concentration \( (c_{\text{max}}) \), and the fraction bound ions \( (p_b) \), see the text. The statistical error in the simulated energy is \( \pm 0.2\% \) and in the other properties \( \pm 2\% \).

### Table II: Convergence of the MC Simulations with the External Potential \( \Phi_e = \Phi_e^{\text{MC}} \) and \( b = 10.5 \text{ Å} \)

<table>
<thead>
<tr>
<th>( N )</th>
<th>( E_{\text{II}} )</th>
<th>( E_{\text{TW}} )</th>
<th>( E_{\text{II} - \text{PB}} )</th>
<th>( E_{\text{II} - \text{PB}} )</th>
<th>( E_{\text{II} - \text{PB}} )</th>
</tr>
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<tbody>
<tr>
<td>20</td>
<td>17.31</td>
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<tr>
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<td>23.61</td>
<td>30.50</td>
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<tr>
<td>150</td>
<td>28.85</td>
<td>26.31</td>
<td>33.40</td>
<td>37.10</td>
<td>40.80</td>
</tr>
</tbody>
</table>

In systems with electrostatic interactions, it is often useful to go beyond the MI approximation. This can be accomplished by making an Ewald-type summation, and, as pointed out by Torrie and Valleau, it is preferable in the present type of system to introduce the effect of the particles that are not explicitly included in the simulation through their average distribution. We have chosen to use the ion distribution of eq 11 predicted by the PB equation for this purpose. Then

\[
\Phi_e^{\text{MC}}(z, \alpha) = \Phi_e^{\text{MC}}(z, \alpha) + \frac{1}{4\pi\varepsilon_0} \int_{\infty}^{\infty} \int_{-\pi}^{\pi} \frac{\rho_{\text{PB}}(z_1)}{\left( x^2 + y^2 + (z - z_1)^2 \right)^{1/2}} \, dx \, dy \, dz_1
\]

where the second term on the right-hand side is due to the charges outside the MC box. To obtain convergence in the integral, it is essential to have an electroneutral system, and \( \rho_{\text{PB}} \) contains also the charges on the walls. The integrations over \( x \) and \( y \) can be performed as in eq 16, whereas the integration over \( z_1 \) has to be made numerically. Values of the integral for different \( z \) values are tabulated in the program for each choice of \( \alpha \) and \( b \). The total energy is with this extension

\[
E_{\text{TOT}} = E_{\text{II}} + E_{\text{TW}} + E_{\text{II} - \text{PB}} + E_{\text{II} - \text{PB}} + E_{\text{II} - \text{PB}} = (U/\text{MC}) + E_{\text{WW}} + E_{\text{WW} - \text{PB}}
\]
Ion Distributions in Lamellar Liquid Crystals


**Figure 2.** Concentration profiles between the two charged plates for mono- and divalent ions. The plate distance $2b = 21.0 \text{ Å}$. The smooth curves are taken from the PB equation and the two others are obtained from MC simulations.

On the basis of these test calculations, a series of simulations were performed in the MIC approximation for varying distances between the plates. The number of particles were chosen to $N = 50$, the displacement parameter was $6 \text{ Å}$, and $2 \times 10^6$ configurations were generated in each case.

**Particle Distribution Functions**

The one-particle distribution function $n(z) \sim c(z)$ was calculated from the MC simulations simply by counting the number of ions in layers parallel to the charged walls. Figure 2 shows a comparison between the concentration profiles obtained from the simulations and from the PB equation for both $Z = 1$ and $Z = 2$. The agreement is surprisingly good considering that the concentration close to the plates is $\sim 15 \text{ M}$. The absolute value of the error, i.e., the difference between the MC and PB results, is largely independent of the electrostatic interaction, it is taken into account within the approximations leading to the PB equation (cf. the second term in the right-hand side of eq 4). The neglect of ion-ion correlations leads to some quantitative changes (vide infra), but it does not change the qualitative picture. It is, for example, clear that ion-ion correlations are more important for divalent than for monovalent ions, which explains the larger discrepancy between the MC and PB approaches in the former case.

In relation to experimental studies of lamellar liquid crystals, there are some properties of the ion distribution that are particularly interesting. In spectroscopic studies of ion binding, it is usually the ions in the close vicinity of the lamellar surface that are studied, and it is thus important to determine how the fraction of ions close to the wall varies with the distance $b$. We have chosen to calculate the fraction of ions, $p_b$, which are within $3 \text{ Å}$ from the walls, and, as seen in Figure 3, $p_b$ reaches an asymptotic value as $b$ is increased. This asymptotic value is slightly larger, and it is reached at a smaller value of $b$ in the MC simulations relative to the PB case, but also for this property there is good agreement between the two methods.

The derivatives $\delta A/\delta b$ and $\delta A/\delta N$ of the free energy are related to the chemical potentials of the solvent and the ions, respectively. Within the PB approximation these derivatives are determined by the ion concentration where the effective force is zero. In the present case this is at $z = 0$. Figure 4 shows a plot of $c(0)$ vs. $1/b^2$ in which the PB solution gives a straight line in the limit of large $b$. Also for the MC case it appears that a straight line is obtained but with a smaller slope. The relatively large discrepancy between the two methods for this property reflects the fact that the relative error in the PB solution is largest at $z = 0$. It appears that the PB equation is less accurate in determining derivatives of the free energy than for other properties of the ion distribution, but a cancellation effect in the full expression for $A$ might invalidate this conclusion.

From Figures 2, 3, and 4, it is clear that the ions accumulate slightly more towards the walls in the MC simulations than in the PB case. The reason is that when one allows for ion-ion correlations as in the MC treatment the near-neighbor repulsions are somewhat less than when $g(r) = 1$. Thus it is possible to concentrate the ions even more closely to the walls. This effect is quite analogous to correlation effects in molecular-orbital calculations where one obtains a contraction of the electron cloud when one goes beyond the Hartree–Fock approximation.

In cylindrical symmetry the pair correlation function $g(r,r')$ depends on three variables, i.e., $g(r,z,x)$, where $r = [(x - x')^2 + (y - y')^2]^{1/2}$. Because of this three-variable dependence, it is computationally difficult to determine...
The pair correlation function for ions in a layer of 1-Å thickness adjacent to either wall ($z = z' = b - 1/2$). The smooth curve is obtained from the Debye-Hückel theory with $\kappa^2 = 1$ Å.

Figure 5. The ratio of the third to the second term in eq 19, calculated from MC data (circles) as described in the text. The curve shows the same quantity but with the first term in eq 19 calculated from the Poisson-Boltzmann equation through $d/dz \ln n_m(z) = (-Ze/kT) d\Phi/dz$.

The two first terms can be evaluated from the MC simulation by numerical derivation and integration, respectively, making it possible to determine the third term from the Debye-Hückel theory with $\kappa^2 = 1$ Å. The smooth curve is obtained from the simulations. To obtain a qualitative picture we have determined $g(r,b)$ in layers 1 Å thick parallel to the walls for the three layers closest to the walls. In Figure 5 $g(r,b=1/2,b=1/2)$ is plotted as a function of $r$. There is a short-range correlation with the same qualitative behavior as in a very concentrated electrolyte solution. No long-range ordering, which would manifest itself as oscillations in $g$, can be seen. This is in accordance with corresponding calculations on plasmas. For the other two layers $g$ does not change relative to that in Figure 5 within the statistical fluctuations.

The short-range character of $h(r,b) = g(r,b)$ provides a justification for neglecting the third term in eq 4. Contributions to the integral come only from a relatively small volume compared to the integral in the second term. Since we cannot compute the full pair correlation function, it is not possible to evaluate the integral explicitly to get a direct measure of the relative importance of the terms in eq 4. However, due to the symmetry the integral $\int \nabla U(r,\tilde{r}) n(\tilde{r}) d\tilde{r}$ can be solved explicitly over $dx'$ and $dy'$ and from eq

$$ -kT \frac{d}{dz} \ln [n(z)] = \frac{Ze^2}{\kappa^2} \int_0^b n(z') d\tau' + \int \nabla U(r,\tilde{r}) n(\tilde{r}) h(r,\tilde{r}) d\tilde{r}' (19) $$

The two first terms can be evaluated from the MC simulation by numerical derivation and integration, respectively, making it possible to determine the third term from eq 19. As shown in Figure 6, the third term in eq 19 is only of the order of a factor of 2 or 3 less than the second term, but it changes sign close to the wall. The accuracy of the calculated $n(z)$ in the PB approximation is thus better than the accuracy in the approximation leading to eq 8 and 9. Apparently a cancellation of errors occurs in the integration of the differential equation. In the PB approximation, we have determined $g(r,b)$ in layers 1 Å thick parallel to the walls for the three layers closest to the walls. In Figure 5 $g(r,b=1/2,b=1/2)$ is plotted as a function of $r$. There is a short-range correlation with the same qualitative behavior as in a very concentrated electrolyte solution. No long-range ordering, which would manifest itself as oscillations in $g$, can be seen. This is in accordance with corresponding calculations on plasmas. For the other two layers $g$ does not change relative to that in Figure 5 within the statistical fluctuations.

The errors in the energy might of course be partly canceled by corresponding changes in the entropy so that the free energy estimated from the PB equation may still be relatively accurate. A strict determination of the free energy and the entropy is unfortunately not possible from the present MC simulations since it requires, for example, simulations at different degrees of charging in the system. However an estimate of these quantities can be obtained by noting that the main contribution, $S_1$, to the entropy comes from the homogeneous distribution of $c(z)$ as in eq 15. The entropy contributions $TS_1' = -T S_1 = -T c(z) \ln c(z)$ are listed in Table IV for the MC and PB cases. The absolute errors in the PB approximation are generally somewhat smaller. The larger values of $-TS_1'$ in the MC simulations, Table IV: Energies, Entropies, and Free Energies as a Function of the Plate Distance $b$

<table>
<thead>
<tr>
<th>$b$, Å</th>
<th>$E_{TOT}$, kJ/mol</th>
<th>$E_{PD}$, kJ/mol</th>
<th>$E_{PB}$, kJ/mol</th>
<th>$A_b$, kJ/mol</th>
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</thead>
<tbody>
<tr>
<td>6.0</td>
<td>-0.95</td>
<td>-0.95</td>
<td>4.17</td>
<td>4.05</td>
</tr>
<tr>
<td>10.5</td>
<td>-0.46</td>
<td>-0.62</td>
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<td>3.24</td>
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<tr>
<td>15.5</td>
<td>-0.20</td>
<td>-0.44</td>
<td>3.12</td>
<td>2.81</td>
</tr>
<tr>
<td>25.0</td>
<td>0.04</td>
<td>-0.26</td>
<td>2.88</td>
<td>2.43</td>
</tr>
<tr>
<td>50.0</td>
<td>0.39</td>
<td>-0.10</td>
<td>2.65</td>
<td>2.09</td>
</tr>
</tbody>
</table>

The statistical error in the MC results is of the order of $\pm 0.1$ kJ/mol. $MC = $ Monte Carlo simulation. $PB = $ Poisson-Boltzmann equation.

Energy, Entropy, and Free Energy

One of the more important applications of the PB equation is in calculations of the electrostatic contributions to the energy and free energy as, for example, in the DLVO theory of colloidal stability. The relative large error in $c(0)$ in the PB approximation indicates, as pointed out in the previous section, that the derivatives of the electrostatic (free) energy also contain substantial error. Table IV shows the variation of $E_{TOT}$ with the distance $b$. In the PB case the energy $E$ goes to an asymptotic value as $E = E_\infty + constant/b$, and it seems that a similar relation holds for the MC simulations with $E_{TOT}(b=\infty) \approx 0.7$ kJ/mol although the statistical uncertainty is substantial. In the PB approach the energies are calculated relative to a reference state which contains only neutral species, which gives a different absolute value of $E$ relative to the MC case. If one equates $E_{PD}(b=6$ Å) with $E_{TOT}(b=6$ Å), the relative changes in the electrostatic energy can be compared for the two methods, and the values of $E_{PD}$ obtained with this reference state are given in the second column in Table IV. It is seen that there is a clearly larger change in energy in the MC simulations than for the PB approximation.

The errors in the energy might of course be partly canceled by corresponding changes in the entropy so that the free energy estimated from the PB equation may still be relatively accurate. A strict determination of the free energy and the entropy is unfortunately not possible from the present MC simulations since it requires, for example, simulations at different degrees of charging in the system. However an estimate of these quantities can be obtained by noting that the main contribution, $S_1$, to the entropy comes from the homogeneous distribution of $c(z)$ as in eq 15. The entropy contributions $TS_1' = -T S_1 = -T c(z) \ln c(z)$ are listed in Table IV for the MC and PB cases. The second term in the parenthesis is due to the entropy of an ideal solution. One can note that in the PB approximation the tabulated values give the total entropy term since ion correlation effects are neglected. In the PB case the entropy term reaches an asymptotic value as $S_1 = constant/b$. The same relation holds, within the statistical fluctuations, also in the MC simulations, but with a slightly smaller slope. The larger values of $-TS_1'$ in the MC simulations,
The policy in the present study is to investigate the consequences of the statistical-mechanical approximations inherent in the PB equation while accepting the physical model. It is clear that a number of features of this model do not apply strictly in real systems. There are thus a number of possible refinements that can be made, e.g., using point charges on the wall, introducing hard-sphere potentials in the ion–ion interaction, allowing for image charge effects, introducing dielectric saturation, or possibly explicitly treating the solvent on a molecular basis, etc. However, a common feature of all of these effects is that they have a short-range character, and it seems possible that the PB equation will still give qualitatively correct predictions about the long-range effects as, for example, illustrated by the asymptotic behaviors of $n(0)$, $p_b$, and $E_{\text{TOT}}$.

**References and Notes**