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 torsional energy levels for CH₃NH₂ based on barrier values reported by Itoh^{37,38} and Lide;³⁹ for this work $V_3 = 691.1$ 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.

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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

Bo Jönsson,[†] Håkan Wennerström, *[†] and Bertil Halle[‡]

Divisions of Physical Chemistry, Chemical Center, S-220 07 Lund 7, Sweden (Received: December 18, 1979)

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 spectroscopic¹⁻⁴ or kinetic^{3,5} experiment or can focus

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[‡]Division of Physical Chemistry 1.

[†]Division of Physical Chemistry 2.



Figure 1. A schematic illustration of the structure of a lyotropic lamellar liquid crystal (lower figure). The amphiphilic molecules form bilayers which are intercalated with aqueous lamellae containing the counterions. The upper figure shows the model of the aqueous region used in the MC simulations.

the attention on the energetic effects of the electrostatic interactions. These influence ion activities,^{6,7} osmotic pressures,^{6,8} macromolecule⁹ or aggregate^{10,11} conformations, phase equilibria,^{12,13} and interparticle forces.¹⁴

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 ioncondensation behavior,¹⁵⁻¹⁷ can be derived from the Poisson-Boltzmann equation,^{7,8,15,18-20} but alternative derivations also exist.^{16,21} There is in general a very good agreement between these predictions about the ion distribution and experimental investigations.^{2,5,17,22,23} For quantities related to energies, the agreement between theory and experiment is somewhat less satisfactory. For phase equilibria^{13,24} the Poisson–Boltzmann equation gives a remarkably good description, whereas for ion activities and osmotic pressures there is qualitative but not quantitative agreement.⁶⁻⁸

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 crystals²⁵ (see Figure 1).

Poisson-Boltzmann Equation for Inhomogeneous Systems

In a statistical-mechanical treatment of ions distributed in a medium of constant permittivity $\epsilon_r \epsilon_0$, the Poisson-Boltzmann equation

$$-\epsilon_r \epsilon_0 \nabla^2 \Phi = \sum Z_\alpha e n_{0\alpha} \exp(-Z_\alpha e \Phi / kT)$$
(1)

is usually derived by assuming that the potential of mean force for an ionic species α is $Z_{\alpha}e\Phi$ where Z_{α} is its valency, *e* the unit charge, and Φ the mean electrostatic potential.²⁶ However, to increase the physical insight and to obtain explicit expressions for the correction terms, we have rederived eq 1 with special emphasis on inhomogeneous systems.

In an inhomogeneous system the one-particle distribution function $n_{\alpha}(\vec{r})$ describes the concentration variation of species α relative to the fixed center. According to the first member of the Yvon hierarchy,²⁷ for the equilibrium particle distribution functions one has

$$-kT\vec{\nabla} \ln \{n_{\alpha}(\vec{r})\} = \vec{\nabla} U_{\alpha}(\vec{r}) + \sum_{\beta} \int \{\vec{\nabla} U_{\alpha\beta}(\vec{r},\vec{r}')\} \frac{n_{\alpha\beta}(\vec{r},\vec{r}')}{n_{\alpha}(\vec{r})} d\vec{r}' (2)$$

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

$$n_{\alpha\beta}(\vec{r},\vec{r}') \equiv n_{\alpha}(\vec{r}) \ n_{\beta}(\vec{r}') \ g_{\alpha\beta}(\vec{r},\vec{r}') \equiv n_{\alpha}(\vec{r}) \ n_{\beta}(\vec{r}')\{1 + h_{\alpha\beta}(\vec{r},\vec{r}')\}$$
(3)

The right-hand side of eq 2 is now split into three terms $-kT\vec{\nabla} \ln \{n_{c}(\vec{r})\} =$

$$\vec{\nabla} U_{\alpha}(\vec{r}) + \sum_{\beta} \int \{\vec{\nabla} U_{\alpha\beta}(\vec{r},\vec{r}\,')\} n_{\beta}(\vec{r}\,') d\vec{r}\,' + \sum_{\beta} \int \{\vec{\nabla} U_{\alpha\beta}(\vec{r},\vec{r}\,')\} n_{\beta}(\vec{r}\,') h_{\alpha\beta}(\vec{r},\vec{r}\,') d\vec{r}\,' (4)$$

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 α at \vec{r} , and the third term is the correction due to particle correlations. If the interaction is purely electrostatic and

$$U_{\alpha\beta}(\vec{r},\vec{r}\,) = \frac{Z_{\alpha}Z_{\beta}e^2}{4\pi\epsilon_{\epsilon}\epsilon_{0}|\vec{r}-\vec{r}\,|}$$
(5)

then the integral

$$\sum_{\beta} \int U_{\alpha\beta}(\vec{r},\vec{r}\,) \ n_{\beta}(\vec{r}\,) \ \mathrm{d}\vec{r}\,' = Z_{\alpha}e \ \Phi_{i}(\vec{r}) \tag{6}$$

where $\Phi_i(\vec{r})$ 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 $g_{\alpha\beta}(\vec{r},\vec{r}') = 1$, the equation can be integrated directly to give

$$n_{\alpha}(\vec{r}) = n_{0\alpha} \exp\{-[U_{\alpha}(\vec{r}) + Z_{\alpha}e \ \Phi_i(\vec{r})]/kT\}$$
(7)

If furthermore one adopts the primitive model for $U_{\alpha}(\vec{r})$ so that $U_{\alpha}(\vec{r}) = Z_{\alpha}e \Phi_{e}(\vec{r})$ for \vec{r} within the volume V, $U_{\alpha}(\vec{r}) = \infty$, otherwise

$$n_{\alpha}(\vec{r}) = n_{0\alpha} \exp\{-Z_{\alpha} e \Phi(\vec{r}) / kT\}$$
(8)

where the total electrostatic potential $\Phi = \Phi_e + \Phi_i$ is the sum of the external, Φ_e , and internal, Φ_i , potentials.

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

$$kT\nabla^2 \ln \{n_{\alpha}(\vec{r})\} = \sum_{\beta} \frac{Z_{\alpha}Z_{\beta}e^2}{\epsilon_r\epsilon_0} n_{\beta}(r)$$
(9)

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 Coloumb type as in eq 5.

(ii) The pair correlation function $g_{\alpha\beta}$ between the mobile ions is constant and unity.

(iii) The interaction between the mobile ions and the fixed center follows the primitive model with an electro-

static term and a hardwall 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 also 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 $h_{\alpha\beta}$, 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-workers^{29,30} 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 interfacial 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 interfacial 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 molecules form 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 bilaver surface is considered as uniformly distributed, the electrostatic potential, Φ_{e} , 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 20

$$\Phi(Z) - \Phi(0) = (2kT/Ze) \ln \{\cos(sz/b)\}$$
(10)

$$\rho(z) = (\epsilon_0 \epsilon_r \ 2kTs^2/Zeb^2)/\cos^2\left(sz/b\right) \tag{11}$$

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

$$s \tan(s) = K = -Z\sigma eb/(2\epsilon_r \epsilon_0 kT)$$
(12)

where σ is the surface charge density on the plates for an electroneutral 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 longrange 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 where the statistical average

$$\langle f \rangle = \frac{\int f(X) \exp(-U(X)/kT) \, \mathrm{d}X}{\int \exp(-U(X)/kT) \, \mathrm{d}X}$$
(13)
$$X = (\vec{r}_1, \vec{r}_2 ... \vec{r}_N)$$

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

$$\langle f \rangle \simeq 1/M \sum_{i=1}^{M} f(X_i)$$
 (14)

and the configurations X_i are sample weighted by the Boltzmann factor $\exp(-U(X_i)/kT)$. 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 \sim 2000 configurations/particle was sufficient to obtain a statistical error of less than one promille 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.³³ 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 dimension $2a \times 2a \times 2b$, 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 (xand 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 8×10^5 configurations and 200 ions was ca. 2 h on a UNIVAC 1100/80 system.

TABLE I: Convergence of the MC Simulations with the External Potential $\Phi_e = 0$ and $b = 10.5 A^{a,b}$

Ν	$E_{\rm II} = E_{\rm TOT}$	$-S_1$	c_{\max}	p_b	
20	13.24	1.20	6.4	0.511	
40	21.85	1.53	7.1	0.544	
80	34.50	2.28	9.0	0.602	
200	60.75	3.05	10.1	0.650	

^a The units for E, S, and c_{\max} are kJ/mol, J/(mol K), and M, respectively. For the definition of the entropy (S_1) , the maximum concentration (c_{\max}) , and the fraction bound ions (p_b) , see the text. ^b The statistical error in the simulated energy is ~0.2% and in the other properties ~2%.

TABLE II: Convergence of the MC Simulations with the External Potential $\Phi_e = \Phi_e^{MI}$ and $b = 10.5 \text{ A}^a$

N	EII	E_{IW}	E _{WW}	E _{TOT}	$-S_{1}$	c _{max}	p_b
30	17.31	-37.84	20.00	-0.53	4.47	12.8	0.719
40	21.25	-45.56	23.79	-0.52	4.54	13.2	0.724
60	28.06	-58.97	30.37	-0.54	4.71	13.4	0.735
80	33.93	-70.59	30.09	-0.57	4.88	13.8	0.743

^a See footnotes in Table I.

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 Φ_e . In the limit of an infinite system, Φ_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 Φ_e .

The computationally simplest choice is to make $\Phi_e = 0$. The result of such a series of simulations is shown in Table I. In this and the forthcoming tables we have chosen to characterize the ion distribution through three parameters: c_{\max} , the concentration of ions within a layer of 0.2 Å from the wall; p_b , the fraction of ions within a distance of 3 Å from the walls; and S_1 , the entropy, relative to an ideal solution, due to the inhomogeneous one-particle distribution defined through eq 15, where \bar{c} is the average con-

$$S_1 = -R \int c \ln c \, \mathrm{d}V + R V \bar{c} \ln \bar{c} \tag{15}$$

centration and $V = 8a^2b$. 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.³³ In this case

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$$\Phi_{e}^{MI}(z,a)$$

$$\frac{\sigma}{4\pi \epsilon_{r}\epsilon_{0}} \sum_{s=1,-1} \int_{-a}^{a} \int_{-a}^{a} \frac{dx \, dy}{[x^{2} + y^{2} + (z + sb)^{2}]^{1/2}} = \frac{\sigma}{4\pi \epsilon_{r}\epsilon_{0}} \sum_{s=1,-1} 8a \ln \left[\frac{[2a^{2} + (z + sb)^{2}]^{1/2} + a}{[a^{2} + (z + sb)^{2}]^{1/2}} \right] - 2|z + sb| \left\{ \arcsin \left[\frac{a^{4} - (z + sb)^{4} - 2a^{2}(z + sb)^{2}}{[a^{2} + (z + sb)^{2}]^{2}} \right] + \frac{\pi}{2} \right\}$$
(16)

This expression is rather complex, but it is evaluated only once for each configuration, which makes the computational effort negligible. The data in Table II show that the total energy E_{TOT} has converged already at N = 30while the properties of the ion distribution are not converged until N = 80. The energy E_{TOT} is calculated as the sum of the ion-ion (E_{II}), the ion-wall (E_{IW}), and the wall-wall (E_{WW}) interactions. E_{WW} , which does not affect the simulation, contains both the interaction between the two walls and the self-energy of the walls.

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, but, as pointed out by Torrie and Valleau,³¹ 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

$$\Phi_{e}^{MIC}(z,a) = \Phi_{e}^{MI}(z,a) + \frac{1}{4\pi \epsilon_{r}\epsilon_{0}} \int_{\pm a}^{\pm \infty} \int_{\pm a}^{\pm \infty} \int_{-b}^{\pm \infty} \frac{\rho_{PB}(z_{1})}{\{x^{2} + y^{2} + (z - z_{1})^{2}\}^{1/2}} dx dy dz_{1}$$
(17)

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 $\rho_{\rm PB}$ 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 a and b. The total energy is with this extension

$$E_{\text{TOT}} = E_{\text{II}} + E_{\text{IW}} + E_{\text{I-PB}} + E_{\text{WW}} + E_{\text{W-PB}} = \langle U \rangle_{\text{MIC}} + E_{\text{WW}} + E_{\text{W-PB}}$$
(18)

where the two last terms are configuration independent. The inclusion of the two correction terms $E_{\text{I-PB}}$ and $E_{\text{W-PB}}$, representing the interaction of external charges with the ions and with the walls, respectively, affects the energy very little, but it improves the convergence with respect to the ion distribution considerably. In fact with these terms included a simulation with 2 ions gives almost the same result as one with 80 ions as seen in Table III, and at N = 20 there is convergence within the statistical fluctuations.

TABLE III: Convergence of the MC Simulations with the External Potential $\Phi_e = \Phi_e^{\text{MIC}}$ and $b = 10.5 \text{ Å}^a$

IADDD III.	$\frac{E_{\text{II}}}{E_{\text{II}}} = \frac{E_{\text{IW}}}{E_{\text{I}}} = \frac{E_{\text{I}}}{E_{\text{I}}} = \frac{E_{\text{W}}}{E_{\text{I}}} = \frac{E_{\text{W}}}{E_{\text{W}}} = \frac{E_{\text{W}}}{E_{\text{TOT}}} = -S_1 = c_{\text{max}} = p_b$									
N	EII	E _{IW}	E _{I-PB}	E _{W-PB}	E_{WW}	$E_{\rm TOT}$	$-S_{1}$	c _{max}	p _b	
2	0.85	-6.41	3.40	-2.22	4.17	-0.21	5.76	14.2	0.781	
6	4.41	-13.22	3.28	-2.50	7.73	-0.30	5.27	14.0	0.758	
20	12.74	-29.18	2.76	-2.39	15.68	0.39	5.03	14.5	0.746	
40	21.24	-45.64	2.31	-2.11	23.79	-0.41	4.90	13.3	0.742	
60	28.03	-59.03	2.02	-1.89	30.37	-0.50	5.01	13.9	0.747	
80	33.94	-70.60	1.82	-1.73	36.09	-0.48	4.95	13.9	0.743	

^a See footnotes in Table I.



Figure 2. Concentration profiles between the two charged plates for mono- and divalent ions. The plate distance 2b = 21.0 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 Å, and 2×10^5 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 ~ 15 M. The absolute value of the error, i.e., the difference between the MC and PB results, is largely independent of z so that the relative accuracy in $c_{PB}(z)$ is much better close to the walls than in the lowconcentration domain. The results in Figure 2 also indicate that the PB approximation becomes slightly less accurate for divalent ions.

It might seem surprising that the ions concentrate close to the walls in spite of the fact that there is no external potential attracting them to the surface, but, as clearly shown by the data in Table I, it is the ions themselves that create the inhomogeneous potential. This effect is wellknown for conductors which always collect their net charge on the surface. The accumulation of counterions close to a charged surface can thus be attributed to the repulsion between the counterions that would occur in the bulk solution if the ions were to be there. This is a general effect, and, since it is due to the long-range character 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,^{1,2,4,17} 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 Å from the walls, and, as seen in Figure 3, p_b reaches an asymptotic



Figure 3. Fraction bound ions, i.e., the fraction of ions within 3 Å from either wall, as a function of *b*. The curve is obtained from the PB equation and the circles are MC results.



Figure 4. The concentrations in the midplane between the plates as a function of $1/b^2$. The curve is from the PB equation and the circles are obtained from MC simulations.

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 $\partial A/\partial b$ and $\partial A/\partial N$ 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.³⁴ 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 $g(\vec{r},\vec{r}') = 1$. 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 $g(\vec{r},\vec{r})$ depends on three variables, i.e., g(r,z,z'), where $r = \{(x - x)^2 + (y - y')^2\}^{1/2}$. Because of this three-variable dependence, it is computationally difficult to determine



Figure 5. 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 $\kappa^{-1} = 1$ Å.



Figure 6. 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 PB equation through $d/dz \ln n^{PB}(z) = (-Ze/kT) d\Phi^{PB}/dz$.

g from the simulations. To obtain a qualitative picture we have determined $g(\vec{r},\vec{r'})$ 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.³⁵ For the other two layers g does not change relative to that in Figure 5 within the statistical fluctuations.

The short-range character of $h(\vec{r},\vec{r}') = g(\vec{r},\vec{r}') - 1$ 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 $\int \{\vec{\nabla} U(\vec{r},\vec{r}')\} n(\vec{r}') d\vec{r}'$ can be solved explicitly over dx' and dy' and from eq 4

$$-kT\frac{\mathrm{d}}{\mathrm{d}z}\ln\{n(z)\} = -\frac{Z^2e^2}{\epsilon_r\epsilon_0}\int_0^z n(z') \,\mathrm{d}z' + \int_{\vec{r}} \{\vec{\nabla} U(\vec{r},\vec{r}')\} n(\vec{r}') h(\vec{r},\vec{r}') \,\mathrm{d}\vec{r}'$$
(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 integra-

TABLE IV: Energies, Entropies, and Free Energies as a Function of the Plate Distance 2b

	$E_{\rm TOT}$, kJ/mol		$-TS_1'$, k	J/mol	A, ^b kJ/mol		
b, Å	MC^d	PB ^{a,e}	MC^d	PB ^e	$\overline{\mathrm{MC}^d}$	PB ^e	
6.0	-0.95	-0.95	4.17	4.05	3.22	3.10	
10.5	-0.46	-0.62	3.48	3.24	3.02	2.62	
15.5	-0.20	-0.44	3.12	2.81	2.92	2.37	
25.0	0.04	-0.26	2.88	2.43	2.92	2.17	
50.0	0.39	-0.10	2.65	2.09	3.04	1.99	

^a The PB energy has been set equal to -0.95 kJ/mol for b = 6.0 A in order to make the comparison with the same reference state (see also in the text). ^b Defined in eq 20. ^c The statistical error in the MC results is of the order of $\pm 0.1 \text{ kJ/mol}$. ^d MC = Monte Carlo simulation. ^e PB = Poisson-Boltzmann equation.

tions of the differential equation. In the PB approximation, where h = 0, eq 19 is the relation between the electrical field and the integrated charge density that follows from Gauss law. It is thus clear that the electrical field is less accurately described in the PB approximation. The relative error in the field from the PB equation is also displayed in Figure 6. As expected, the two curves in Figure 6 behave similarly, but the error in the PB field is somewhat smaller.

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.¹⁴ The relatively 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_{∞} + constant/b, and it seems that a similar relation holds for the MC simulations with $E_{\text{TOT}}(b \rightarrow \infty) \simeq 0.7 \text{ kJ/mol}$ 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 $E_{\rm PB}(b=6\,{\rm \AA})$ with $E_{\rm TOT}(b=6\,{\rm \AA})$, the relative changes in the electrostatic energy can be compared for the two methods, and the values of $E_{\rm PB}$ 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 inhomogeneous distribution in c(z) as in eq 15. The entropy contributions $TS_1' = -T(S_1 - R \ln \bar{c})$ 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 $S_1 = S_{1\infty} +$ 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 are another manifestation of the fact that the charge distribution is more contracted in the simulations than in the PB case.

An estimate of the Helmholtz free energy can be made through eq 20, and the values of A are given in the last two

$$A = E - TS_1' \tag{20}$$

columns of Table IV. There is a cancellation effect so that the changes in A are smaller than in E and TS'. As a result the statistical errors in the simulations become of the same order of magnitude as the changes in A, making it impossible to obtain reliable estimates of $\partial A/\partial b$. However, the general trend is that A depends less on b in the simulations than in the PB solution, although the changes are so small that it is likely that higher-order contributions to the entropy could change this qualitative picture.

Conclusions

The validity of the statistical-mechanical approximations inherent in the Poisson-Boltzmann equation have been assessed by comparing the PB solution with results from Monte Carlo simulations. The PB equation is derived from the Yvon hierarchy of particle distribution functions by neglecting the correlations between the mobile ions. For a system of equally charged ions between two charged plates, the PB equation provides a good approximation of the statistical-mechanical problem with respect to the particle distribution in agreement with several recent findings.²⁸⁻³¹ The problems concerning the consistency of the nonlinearized PB equation discussed in many textbooks is thus greatly exaggerated when the equation is applied to a polyelectrolyte system.

This conclusion is arrived at by comparing the ion distributions in the PB and MC treatments and by explicitly calculating the correction term. The largest relative error appears for the concentration c(0), which is significant, since in the PB treatment this concentration is directly related to the activities of the ions and the solvent. Even when there is a discrepancy in quantitative terms, the PB solutions seem to give the right asymptotic behavior when the distance between the plates is increased. This is demonstrated for the concentrations c(0), for the concentration close to the plates as measured by p_b , and for the total energy.

In the MC simulations, where one allows for the correlations between the particles, the ions can accumulate even more closely to the surface, since the repulsions between the particles are lowered on a short-range scale through the correlations. That the pair correlations actually are of a short-range type is shown by determining the correlation function for the ions close to the plates. For the case of uniformely charged parallel plates, there is no external force that attracts the ions to the surface, and it is thus clear that the accumulation of ions close to the plates is due to the repulsion between the ions themselves. This is a rather general effect, and it also applies in the presence of a salt and also for the interior of a spherical vesicle. The accumulation of ions close to a polyelectrolyte can then be understood as due to the inability of the bulk solution to sustain a net electrical charge even over moderately large distances.

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 $E_{\rm TOT}$.

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