Counterion release and interaction of oppositely charged surfaces

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The interaction of two oppositely highly charged surfaces in an electrolyte solution and the number of released counterions from the slit between the surfaces were studied in terms of the anisotropic hypernetted chain and nonlinear Poisson-Boltzmann theories. Liquid theory predictions of the attractive pressure and release of counterions between the plates are larger than those of the mean field approach at low and moderate concentration of added salt. Further, at high salt concentration there is an opposite relationship of the two theories in their numerical results for the attractive pressure for all surface separations. These deviations of the predicted equilibrium properties arise both from the charge density and the ion size correlation effects included in hypernetted chain theory.

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I. INTRODUCTION

Counterion release is a mechanism for attraction among charged biopolymers in aqueous solvents [1,2]. Wagner *et al.* [3] determined experimentally the amount of counterions released upon DNA and cationic liposome (CL) self-assembly in aqueous solution. They found that the DNA-CL condensate formation is driven by the large counterion entropy increase that originates due to translation of counterions into the bulk of the solution from their previously formed double layers around each single uncondensed macromolecule.

Wagner *et al.* found good agreement between their experiments on the amount of counterion released and their comprehensive calculations for this thermodynamic property using nonlinear Poisson-Boltzmann (PB) theory. In recent years, Meier-Koll *et al.* [4] studied with numerical solutions of the PB equation the effect of counterion release on the effective interaction of two oppositely charged planar surfaces having a smooth distribution of surface charges which interact through an electrolyte solution modeled by pointlike ions. They found that the release of ions becomes important at high charge plate and low salt concentrations. More recently, Safran [5] considered the same model system as Meier-Koll *et al.* and derived within PB theory analytical scaling relations for the fraction of released counterions and the attractive pressure of the charged surfaces as a function of the electric field at midplane distance.

In many real cases, the surfaces of the macromolecules have a discrete distribution of charges as found in ionic surfactant bilayers. Yet the presence of salt ions in solution induces positional correlations among the different charged species that affect the overall structural thermodynamic properties such as the number of released counterions from the system and the surface interactions. In this paper we study with the help of the anisotropic hypernetted chain (AHNC) liquid theory [6] the influence on the ion excess, total pressure, and profile distribution of ions from the surface, due to charge-charge density correlations and liquidlike distribution of discrete surface charges at both low and high electrolyte concentration. We take into account the finite ionic size and compare liquid theory with mean field PB

results on the same equilibrium properties. We found that PB theory always underestimates the fraction of released ions and the attractive pressure between the surfaces for low concentration of electrolyte. It agrees with AHNC theory at small plate separations. However, mean field theory yields a larger attractive pressure than AHNC at high salt concentration. Using liquid theory we found that a smeared out charge on surfaces leads to small quantitative differences in the above mentioned thermodynamic properties, with respect to a discrete distribution of surface charges. The former case predicts a stronger attraction than the latter. In all cases studied the largest surface attractive pressure and counterion release occurs for the system with lower bulk concentration of added salt in solution.

II. MODEL SYSTEM AND THEORY

Figure 1 depicts a system constituted of two surfaces with equal magnitudes of surface charge $|\sigma_s|=0.267$ C/m^2 and of
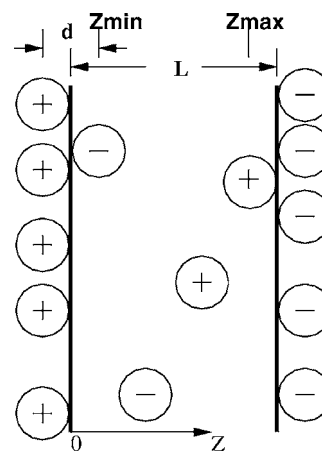

FIG. 1. Two oppositely charged surfaces separated by a distance L immersed in a simple electrolyte solution. Shown is a discrete density of surface charge $|\sigma_s|=0.267$ C/m^2 on each plate. The salt ions and surface charges are formed by spheres of diameter $d=4.25$ Å.

opposite sign. The surfaces are separated by the distance L by an intervening simple 1:1 electrolyte in water of dielectric constant $\epsilon = 78.5$. In the aqueous phase all ions have the same hydrated diameter $d = 4.25$ Å; therefore, the source field generated by an ion of species i at a distance r_{3D} is

$$u_i(r_{3D}) = \begin{cases} \dfrac{q_i}{\epsilon r_{3D}}, & r_{3D} > d, \\ \infty, & r_{3D} < d, \end{cases} \quad (1)$$

where a hard core has been included to avoid overlapping between spheres and we defined $r_{3D} = \sqrt{r^2 + z^2}$. $q_i = ev_i$ is the charge on sphere i, with $v_i = \pm 1$ being its valence and e being the elementary charge. r is the radial distance on one surface from the ion to the origin of coordinates. For the case of surfaces bearing discrete charges we consider that each plate has a liquidlike distribution of these same size spheres. We shall not consider image charge effects. At thermal equilibrium the microstructure of such a system is obtained from the Ornstein-Zernike equation [7]

$$h_{ij}(r,z_1,z_2) = c_{ij}(r,z_1,z_2) \\ + \Sigma_\gamma \int d\mathbf{r}\, dz_3 c_{i\gamma}(r,z_1,z_3) n^\gamma(z_3) h_{\gamma j}(r,z_3,z_2), \quad (2)$$

where the total correlation function $h_{ij} = g_{ij} - 1$ and the direct correlation functions c_{ij} are given self-consistently through the AHNC closure relation

$$g_{ij}(r,z_1,z_2) = \exp[h_{ij}(r,z_1,z_2) - c_{ij}(r,z_1,z_2) - \beta u_i(r_{3D})q_j], \quad (3)$$

with g_{ij} being the pair correlation function. $\beta = 1/k_B T$, and k_B is the Boltzmann's constant and $T = 298$ K is the temperature. The profile distribution of ions in the normal direction to the surfaces is determined from [6,8]

$$n^i(z_1) = \frac{e^{\beta \mu^i}}{\Lambda_i^3} \exp\left[-\beta q_i \psi(z_1) - \Sigma_j \int d\mathbf{r}\, dz_2 n^j(z_2) \right. \\ \times \left(\frac{1}{2} h_{ij}^2(r,z_1,z_2) - c_{ij}(r,z_1,z_2) - \beta u_i(r,z_1,z_2)q_j \right) \\ \left. + \frac{1}{2}[h_{ij}(0,z_1,z_1) - c_{ij}(0,z_1,z_1)] \right], \quad (4)$$

where μ^i is the chemical potential, which in thermodynamic equilibrium reaches a constant value, while $\Lambda_i \equiv \Lambda$ is the thermal wavelength of ion i, which is assumed to be the same for all ionic species. In the above equation

$$q_i \psi(z_1) = -4\pi \frac{q_i}{\epsilon} \sigma_s\left(z_1 - \frac{L}{2}\right) - 2\pi \frac{q_i}{\epsilon} \Sigma_j \int dz_2 |z_1 - z_2| n^j(z_2) q_j, \quad (5)$$

where $\psi(z_1)$ is the average electric field in the electrolyte phase at position z_1 [6]. The converged solution of Eq. (2) is obtained self-consistently with the help of Eqs. (3)–(5) and using a cut of the long-range tail in h_{ij} and c_{ij} that originates from the Coulomb potential [7], until the difference of two consecutive solutions is less than 0.01%. In all our numerical results for AHNC theory, the overall electroneutrality condition on the system (see Fig. 1) was imposed:

$$\int_{z_{\min}}^{z_{\max}} dz[+en^+(z) - en^-(z) + \sigma_s - |\sigma_s|)] = 0, \quad (6)$$

through which we made an exact match of the different ion's chemical potentials that result from the ionic equilibrium with the saline solution; thus, $\mu^+ = \mu_\pm^{\text{bulk}} + \chi$ and $\mu^- = \mu_\pm^{\text{bulk}} - \chi$ with $\exp[\beta \mu_\pm^{\text{bulk}}] = n_0 \Lambda^3 \gamma_\pm$, and $\gamma_\pm$ is the mean activity coefficient corresponding to the concentration n_0 of electrolyte in the reservoir solution. The constant χ is obtained self-consistently from the above equation (6).

At mean field level, we have taken into account finite ionic size effects in the Poisson-Boltzmann equation

$$\nabla^2 \psi(z_1) = -\frac{4\pi}{\epsilon}[+en^+(z_1) - en^-(z_1)], \quad (7)$$

where the ion's concentrations are given by

$$n^\mp(z_1) = \frac{n_0 e^{\pm \beta e \psi(z_1)}}{1 - 2n_0 d^3 + 2n_0 d^3 \cosh(\beta e \psi)}, \quad (8)$$

according to the theory developed in Ref. [9] to include short-range excluded volume interactions in the PB equation. Yet the ion's size restricts them to reach the distance of closest approach $z_{\min} = d/2$ and $z_{\max} = L - d/2$ from the plates.

From Eqs. (4) and (8) the contact (cont) values of the volume distribution of ions $n_{\text{cont}}^\mp(z_{\min})$ are obtained. Therefore, the total (tot) pressure between the walls can be written as

$$P_{\text{tot}} = P_{\text{slit}} - P_{\text{bulk}}, \quad (9)$$

with $P_{\text{slit}} = k_B T(n_{\text{cont}}^+ + n_{\text{cont}}^-) - \sigma_s^2 / 2\epsilon$ from the contact value theorem [10,11], and the osmotic pressure due to the electrolyte solution $P_{\text{bulk}} = k_B T \phi(n_0^+ + n_0^-)$, where ϕ is the bulk osmotic coefficient associated with the ionic bulk density correlations included in the general AHNC framework; meanwhile in mean field theory $\phi = 1$, and $n_0^\mp$ are the bulk densities of both species of ions.

III. RESULTS AND DISCUSSION

Figure 2 shows the comparison of the AHNC (continuous and dashed lines) and PB (dotted line) theories for the profile distribution $n^\mp(z)$, obtained from Eqs. (4) and (8), of negative and positive ions in the slit between the surfaces of Fig. 1. According to Fig. 2 AHNC theory predicts, for a discrete distribution of surface charge σ_s [continuous line in Figs. 2(a) and 2(b)], a higher concentration of ions of the electrolyte both at contact and close to the charged surfaces than in the case of smeared out surface charges (dashed line obtained with AHNC theory, and dotted line from PB theory) at low salt concentrations, as is exemplified in Fig. 2(a) for $n_0 = 0.01M$ of NaCl with corresponding $\gamma_\pm = 0.902$ [12] and given surface separation $L = 9$ Å. On the other hand, the prediction of AHNC and PB theories for smeared out surface charges and salt concentration $n_0 = 0.01M$ lead quantitatively
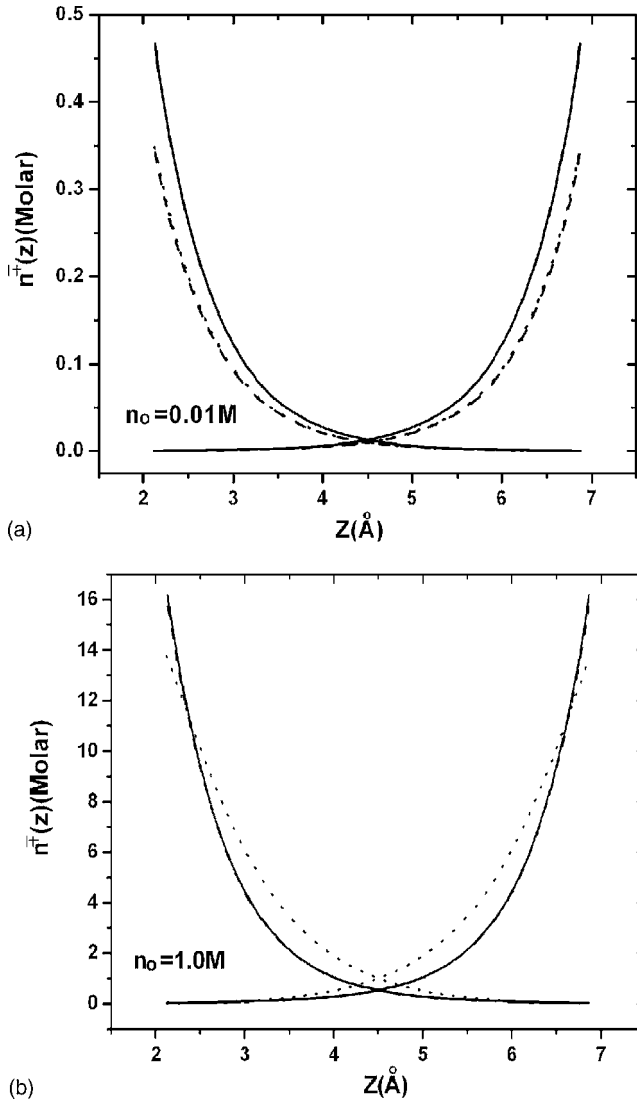
FIG. 2. Local density of negative $n^-(z)$ and positive $n^+(z)$ ions in the slit between the charged surfaces separated a distance L =9.0 Å. Solid curve corresponds to AHNC liquid theory prediction with discrete surface charge $|\sigma_s|=0.267$ C/m^2, and dashed curve is for smeared out σ_s. Dotted curve is the Poisson-Boltzmann result for smeared out surface charge. (a) Corresponds to $n_0=0.01M$ NaCl in aqueous solution, (b) for $n_0=1.0M$ NaCl.

to the same profile distribution of ions. In a previous work [13] we reported also an observed increase in the ion contact densities $n(z_{min})$, as compared to a smooth surface charge distribution, in the case of equally charged and symmetric plates, due to positional correlations among the bulk ion densities with those discrete charges located at the surfaces.

At the highest salt concentration studied, $n_0=1.0M$, AHNC theory predictions are comparable in their magnitudes for any case of surface charge model distribution and yield approximately equal values of the mobile ion's distribution $n^{\mp}(z)$ as shown in Fig. 2(b). Thus, the contact value of the ion's densities is $n^-_{AHNC}(z_{min})=16.16M$ for discrete surface charge and turns out to be of the same order of magnitude $n^-_{AHNC}(z_{min})=15.70M$ for smooth surface charge [whereas mean field theory yields $n^-_{PB}(z_{min})=13.77M$].

Meanwhile, at the midpoint between the surfaces $n^-_{AHNC}(z_{mid})=0.53M$ for discrete σ_s and $n^{\mp}_{AHNC}(z_{mid})=0.52M$ for the continuous surface charge case [with mean field value $n^-_{PB}(z_{mid})=1.0M$]. Therefore, as is known, PB theory always yields at $z_{mid}=4.5$ Å the same concentration as in the bulk solution, and the AHNC approximation predicts in general a different ionic concentration at the midpoint between the plates due to charge-charge correlation and hard core size effects. The above observed quantitative differences between the two approaches used to study the ion distributions $n^{\mp}(z)$ have important effects on the surface-surface interaction according to Eq. (9), since its magnitude depends on the contact values of those bulk ion distributions as will be shown below. In Fig. 3(a) are displayed the results for the slit pressure P_{slit} between the surfaces as determined from the AHNC approximation (continuous and dashed lines) and PB theory (dotted line) at two bulk electrolyte concentrations n_0 =(0.01, 0.1)M. This pressure is not to be confused with the total pressure of Eq. (9) whose value will be given in the Fig. 4(a). Figure 3(a) provides the attractive pressure between the two surfaces as a function of the surface separation L.

From Fig. 3(a) we observe several effects in the pressure curve P_{slit} versus L when increasing the concentration of salt n_0. First, we note that at the lowest salt content considered $n_0=0.01M$ the curve of P_{slit} as obtained from PB theory coincides quantitatively with the AHNC results over the largest range of spatial surface separation $4.25 \leq L \leq 12.5$ Å, with respect to the other cases where the concentration of salt is higher. Thus, for instance, this spatial surface separation is $4.25 \leq L \leq 9.0$ Å for $n_0=0.1M$, and becomes even smaller $4.25 \leq L \leq 6.5$ Å at the highest electrolyte concentration n_0 =1.0M, as seen through the plot of the total pressure P_{tot} [see Fig. 4(a) where we used $\phi \approx 1.094$ [14]]. Note also that at the lowest salt concentration $n_0=0.01M$ there appear the largest deviations in the predicted strength of P_{slit} between the PB and AHNC theories for $L \geq 12.5$ Å, whereas at higher n_0 such deviations between the results of both theories get smaller. This can be seen from the plots of P_{slit} provided in Fig. 3(a) for $n_0=0.1M$, and in Fig. 4(a) where there appear those pressure curves P_{tot} corresponding to $n_0=1.0M$. We observe also from Fig. 3(a) that from low $n_0=0.01M$ up to moderate concentration $n_0=0.1M$ the predicted mean field attractive pressure is underestimated as compared to that from AHNC liquid theory. Whereas at very high salt concentration $n_0=1.0M$ the attractive pressure between the surfaces is predicted by AHNC theory to be of smaller magnitude than mean field theory. For this high concentration of electrolyte we found that the AHNC theory gives qualitatively the same curve of P_{tot} versus L for any case of surface charge distribution, while the mean field result starts to disagree with AHNC for $L>8$ Å. A last remark concerning the pressure curves plotted in Figs. 3(a) and 4(a) refer to the maximum strength they show at the closest distance of surface approach we considered, $L=4.5$ Å (recall the minimum possible value of $L=4.25$ Å, that is, one ionic diameter) where the maximum strength shown by the attractive pressure P_{slit} drops from $P_{slit} \approx -20.66M$, to $-20.44M$, and to $-18.56M$ for increasing $n_0=0.01M$, and $0.1M$, up to $1.0M$ NaCl, with $\gamma_{\pm}=(0.902, 0.778, 0.656)$ [12], respectively. This effect is ex-
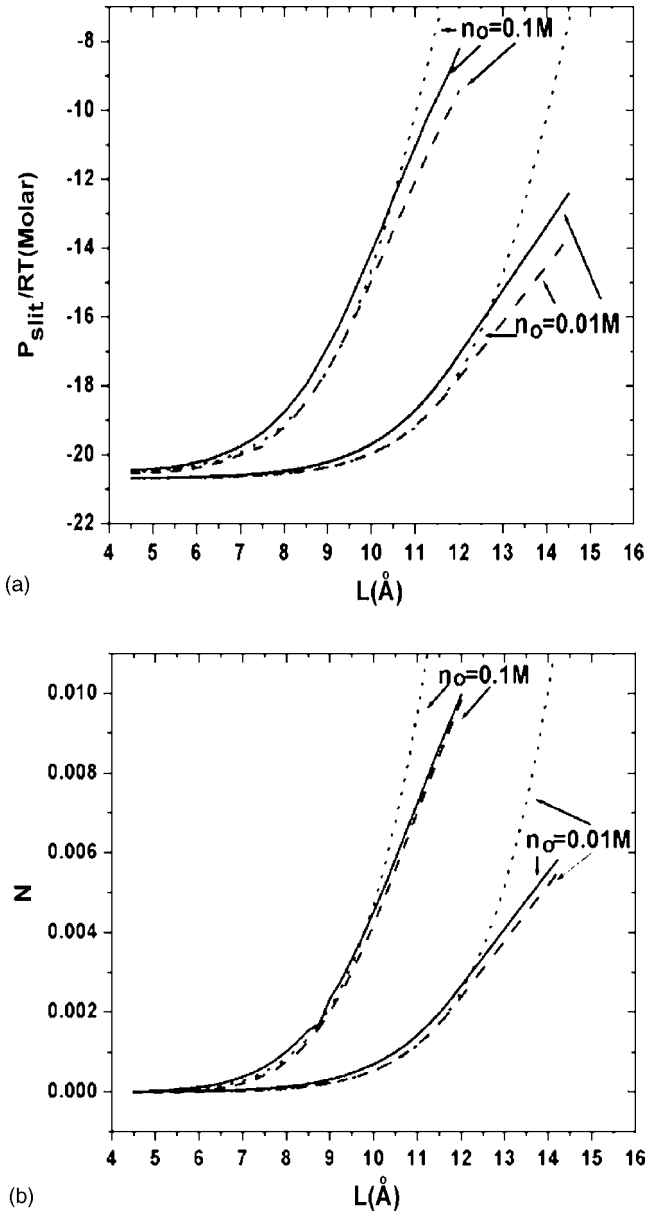
FIG. 3. (a) Slit pressure P_{slit} between the two plates at two concentrations of NaCl versus the surface separation L. Solid curve is AHNC theory with discrete density of surface charge, dashed curve is AHNC theory with smeared out σ_s, and dotted curve is the mean field PB result with smeared out σ_s. (b) Number of released couterions per Å^2 versus L at two bulk salt concentrations n_0: moderate $n_0=0.1M$ and low $n_0=0.01M$. Type of curve same as in (a).

FIG. 4. (a) Total pressure P_{tot} between the two plates as a function of surface separation L at high salt concentration $n_0=1.0M$. (b) Number of released counterions per Å^2 versus L at $n_0=1.0M$. Type of curve as described in Fig. 3.

pected since as the salt concentration increases there remains a finite amount of salt ions located in the slit between the surfaces that screen the surface interaction. We have found from the plots of several bulk ion concentrations versus L like those depicted in Fig. 2 that, as the surfaces approach each other, then the spatial distribution of the ions gets similar to their distribution in the bulk. That is, ions become more homogeneously distributed in the slit between the surfaces; thus, $n^{\mp} \approx n_0$. Therefore, we can observe that there occurs the largest release of counterions $N=\int_{Z_{\min}}^{Z_{\max}} dz(n^+ + n^- - 2n_0) \approx 0$ [see Figs. 3(b) or 4(b)] since the bulk term $2n_0$

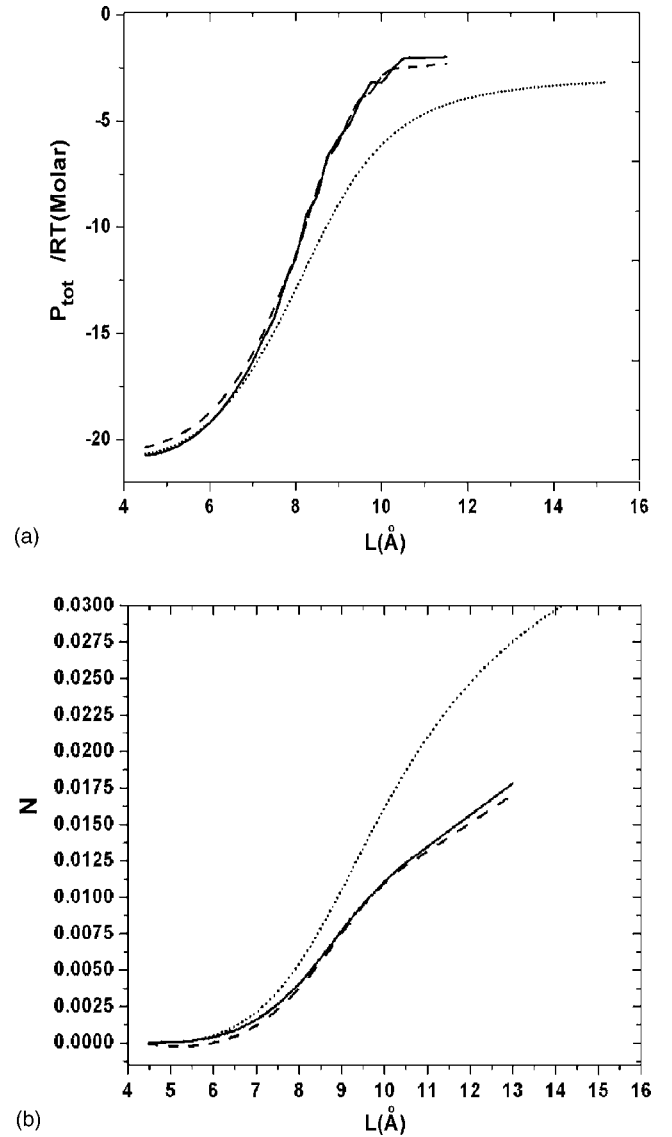cancels the ion density contributions $n^+ + n^-$. Consequently, as the surfaces approach their minimum separation $L=4.25$ Å, they neutralize each other, and counterions and salt ions are released into the bulk solution. Thus, $n_{\text{cont}}^{\mp}$ decreases; therefore, the bulk pressure P_{bulk} cancels the concentration-dependent contribution in $P_{\text{slit}}=k_B T(n_{\text{cont}}^+ + n_{\text{cont}}^-) - \sigma_s^2/2\epsilon$, resulting in the maximum attractive pressure $P_{\text{tot}} \approx -\sigma_s^2/2\epsilon$, that is, $P_{\text{tot}}/RT \approx -20.69M$, the interaction between two unscreened charged surfaces where all counterions have escaped to the reservoir. This approximate expression remains valid also in the interesting region of close approach $0.0 \leq L \leq 8$ Å [equivalently we can see it through the plot of P_{slit} in Fig. 3(a) where it remains flat and approximately constant] for $n_0=0.01M$ where there occurs the largest release of counterions [see Fig. 3(b)], while, for large distances of separations $L>8$ Å and the same small salt concentration, the

quantity N remains finite and different from zero according to AHNC and PB theories.

In general, mean field results predict a smaller amount of released counterions than liquid theory for any concentration of added electrolyte in solution, and there is agreement between both theories just in the close region of a few ion diameters of surface separation. At moderate and low salt content n_0 in solution, PB theory predicts smaller attractive pressure between the surfaces than liquid theory does, while at high n_0 this pressure relationship gets inverted. We found that the largest surface attractive pressure and counterion release occur for the system with lower bulk concentration of salt in solution (Fig. 3).

IV. CONCLUSIONS

In this paper we have made a comparison between the predictions of liquid and mean field theories for the attractive interaction of two asymmetric charged surfaces and the number of their counterions released from the ionic solution in the slit between the plates. Since liquid theory takes into account the charged ion density and size correlation effects, it leads to a larger surface attractive force than mean field theory at low and moderate concentration of electrolyte in the reservoir solution, and there appears an opposite pressure relationship at high salt concentration. If there is a discrete surface charge distribution the strength of the surface interaction is predicted by liquid theory to be of larger magnitude than for the smeared out surface charge density case. Furthermore, we still found the same small quantitative differences between the two theoretical approaches for the number of released counterions. However, there is quantitative coincidence between AHNC and PB theories in their predictions of such thermodynamic properties for very short surface separations of just one or three ion diameters.

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