PHYSICAL REVIEW E VOLUME 53, NUMBER 1 JANUARY 1996

Violation of the electroneutrality condition in confined charged fluids

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(Received 1 August 1995)

The three point extension to the hypernetted chain–mean spherical theory of liquids is solved for a system formed by two charged plates immersed in a restricted primitive model electrolyte, under several boundary conditions. It is shown that the charged fluid confined by the plates and in equilibrium with a reservoir does not necessarily satisfy the local electroneutrality condition. This depends on the boundary conditions imposed on the plates. The whole system, however, does satisfy a general electroneutrality condition. The plate-plate force is calculated and compared to that from existing Monte Carlo simulations.

PACS number(s): 61.20.Qg, 61.20.Gy

I. INTRODUCTION

Important examples of classical charged fluids are condensed classical plasmas, electrolyte solutions, complex fluids, and confined charged fluids. These systems are, overall, electroneutral. However, in a volume element sufficiently close to, say, one of the particles of the system, one can assume this volume element not to be electroneutral. That is, the particles with an opposite charge to that of the central particle do not cancel the central particle's charge. A clear example is that of a lyophobic colloidal dispersion. The knowledge of the net charge in this volume element is important in quasiparticle's models. In inhomogeneous charged fluids, such as a two species electrolyte next to a charged electrode, there is a charge profile, i.e., the counterions' concentration is higher next to the electrode, while the concentration of particles with the same sign to that of the electrode coions is lower. The concentration of both species of particles become equal in the bulk. However, if this charge distribution is integrated from the electrode's surface to a point in the bulk, the net charge obtained cancels exactly that on the electrode. In the chemical physics of charged liquids this charge distribution is known as the electrical double layer (EDL). In confined fluids, for example, electrolyte solutions confined in a slit pore, one can intuitively assume that the EDL inside the pore will not, in general, cancel the charge on the inside surfaces of pore, while the EDL on the outside of the pore will cancel the charge on the external surfaces of the pore plus the charge on the internal surfaces which was not canceled by the inside EDL. An obvious case is that when the slit gap is too narrow to allow ions to get inside the pore [1]. In this case there is no inside EDL and the external EDL will cancel the charge on the whole slit pore. In the field of colloidal dispersions two types of boundary conditions are used to model the interaction of two colloidal particles: (i) constant potential and (ii) constant charge. In the constant potential case, the surface potential on both walls of the slit pore is fixed and is assumed to be independent of the slit's width. In the constant charge case, the surface charge on the slit's walls is fixed and assumed to be independent of the slit's width. If the constant potential boundary condition is chosen, it has been shown that a local electroneutrality condition (LEC) is always satisfied inside the pore [1,2], i.e., the EDL inside the plate cancels the charge on the surfaces inside the pore and the external EDL cancels that on the surfaces outside the pore. If the constant charge boundary conditions are chosen, no general statement can be shown; other than a general electroneutrality condition (GEC), i.e., the inside plus the outside EDL's cancels the total charge on the slit pore [2]. A similar statement can probably be made for fluids confined by pores of different geometries; for example, cylindrical or spherical pores. However, in the literature a LEC for constant charge boundary conditions has been assumed, i.e., in Monte Carlo (MC) [3–8], integral equation [9–15], density functional [16–19], and semiphenological theories [20,21] studies.

An important example of a confined charged fluid is that of an electrolyte solution confined by two charged, parallel plates fixed at a distance τ of each other. A large number of experimental results for the force between these two charged plates have been performed in the past by a several authors, noticeably by Pashley and Israelachvili [22,23]. A widely used model for this system is that of a charged slit immersed into a restricted primitive model electrolyte (RPM). In this model the electrolyte is assumed to be a fluid of charged hard spheres of charge ez_i and diameter a, in a dielectric continuum of dielectric constant ε. Where e is the electronic charge and z_i is the valence of an ion of species i. The plates of the slit are considered to be flat, parallel, hard walls with a surface charge density σ_{in} on the inside surfaces of the slit and a surface charge density σ_{out} on the exterior surfaces of the slit. The walls of the slit have a width d and are com-

1063-651X/96/53(1)/522(9)/$06.00

posed of a dielectric material with a dielectric constant chosen to be equal to that of the solvent, for simplicity, such that image forces need not be considered (see Fig. 1). The electrolyte confined by the slit is in chemical equilibrium with the bulk electrolyte. The two plates are equally charged, i.e., the charge on the two plates have the same sign and magnitude. This is a model useful for biological and colloidal systems. This model or similar models have been studied through computer simulations by various authors [4–8]. However, to have a better understanding of the physics of this system, grand-canonical Monte Carlo simulations (GCMC) are needed. The GCMC simulations of Valleau, Ivkov, and Torrie [8] are particularly useful.

The electroneutrality condition for charged interfaces states that the bulk electrolyte provides the necessary number of coions and counterions to cancel the electrical field produced by a given surface; for example, a single, planar electrode. As a result an ionic concentration profile is produced near the surface, i.e., an EDL is produced. In thermodynamical equilibrium the structure of the EDL is such that the chemical potential of the ionic fluid is a constant throughout all the fluid, i.e., in the bulk electrolyte and near the surface.

In the past, a general approach to study homogeneous and inhomogeneous liquids has been proposed [1,2,24–27]. In this approach, a liquid theory can be systematically improved by progressively including more bridge diagrams. The first order approximation of this perturbationlike theory is the so-called three point extension (TPE). In particular the three point extension to the hypernetted chain–mean spherical approximation (TPE-HNC-MSA) has been successfully applied to study of the interaction of two plates [2,25–27]. In our previous work we have applied the TPE-HNC-MSA equation to the interaction of two plates for constant potential boundary conditions. In this paper we solve the TPE-HNC-MSA equation for constant charge boundary conditions. We show that for these boundary conditions the LEC is violated; that is, the ionic fluids inside the slit do not cancel the charge on the inside surfaces of the plates. We show that the boundary conditions used in the literature, as constant charge boundary conditions, because they force the LEC to be valid, are really constant potential boundary conditions. In Sec. II we outline the TPE-HNC-MSA theory, mathematically define the LEC, and discuss different boundary conditions. In Sec. III we show our results and compared them with GCMC results. In Sec. IV we give some conclusions.

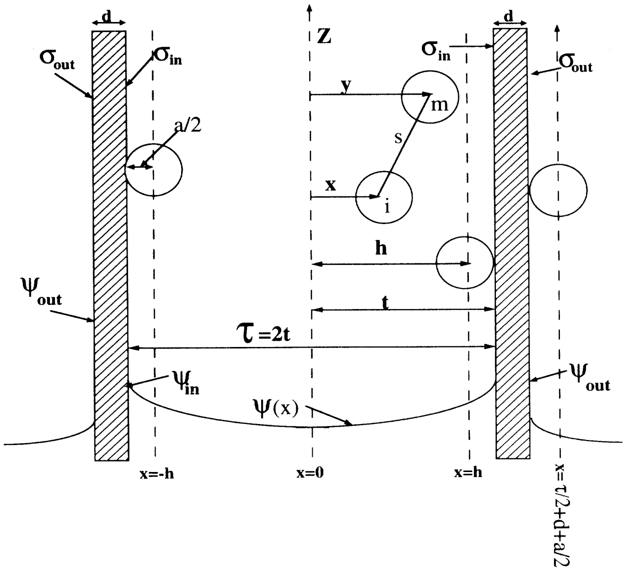

FIG. 1. Geometry for a charged slit immersed in a restricted primitive model electrolyte.

II. THEORY

The TPE-HNC-MSA equation for the interaction of two charged plates immersed into a two species RPM electrolyte is [2]

$$g_{\alpha i}(x)=\exp\left\{-\beta u_{\alpha i}(x)+\sum_{m=1}^{2}\rho_m\int c_{im}(s)h_{\alpha m}(y)dv_3\right\}, \tag{1}$$

where ρ_m is the bulk concentration of the ions of species m; $c_{im}(s)$ is the MSA direct correlation function for ions of species i and m, a distant s apart; $\rho_i g_{\alpha i}(x)$ is the local concentration of ions of species i, at a distance x perpendicular to the midplane between the two walls of the slit; $h_{\alpha m}(y)$, defined as $h_{\alpha m}(y)\equiv g_{\alpha m}(y)-1$, is the total correlation function; dv_3 is the volume differential; $\beta\equiv 1/kT$, where k is the Boltzmann constant and T is the system temperature; $u_{\alpha i}(x)$ is the direct interaction potential between an ion of species i and the slit, represented by the subindex α. For our model, this potential can be separated into a hard sphere–hard wall term, $u^{*}_{\alpha i}(x)$, and an electrostatic part $u^{\mathrm{el}}_{\alpha i}(x)$. The hard sphere–hard wall potential simply takes into account the fact that the ions can not penetrate to deform the walls. From Gauss law, the electrostatic potential can be found to be

$$-\beta u^{\mathrm{el}}_{\alpha i}(x)=\frac{2\pi\beta e z_i}{\varepsilon}[(x+\tau/2+d+|x-\tau/2-d|)\sigma_{\mathrm{out}}+(x+\tau/2+d+|x-\tau/2-d|)\sigma_{\mathrm{in}}] \tag{2}$$

for $0\le x<\tau/2$ and $\tau/2+d<x$. Equation (1) is a nonlinear integral equation that we solve numerically with advanced finite element techniques. The solution of Eq. (1) gives the concentration profile $\rho_i g_{\alpha i}(x)$ inside and outside the slit. This concentration profile satisfies the condition of chemical equilibrium. That is, there is a constant chemical potential throughout all the solution.

The charge distribution in the solution, around and inside the slit, is given by $\rho_{\mathrm{el}}(x)=\sum_{m=1}^{2} e z_m \rho_m g_{\alpha m}(x)$. With this charge distribution function the Poisson equation,

$$\nabla^2\Psi(x)=-(4\pi/\varepsilon)\rho_{\mathrm{el}}(x), \tag{3}$$

can be solved, in terms of $\rho_{\mathrm{el}}(x)$, for various boundary conditions. While many different boundary conditions are possible, two cases are often explored in the study of plates interaction: $\sigma_{\text{in}}=\sigma_{\text{out}}=\text{const}$, independent of τ, referred to as constant charge case, and $\Psi_{\text{in}}=\Psi_{\text{out}}=\text{const}$, independent of τ, referred to as constant potential case. Ψ_{in} and Ψ_{out} are the electrostatic potential on the inside and outside surfaces of the slit, respectively.

The general electroneutrality condition for the slit plus the electrolyte system states that the charge induced in the liquid, by the slit, must cancel that on the slit; that is, $\sigma_{\text{in}}+\sigma_{\text{out}}=-\sigma'_{\text{in}}-\sigma'_{\text{out}}$, where σ'_{in} and σ'_{out} are the induced charges in the liquid between the plates and outside the plates, respectively. Mathematically this condition is expressed as [1,2]

$$\sigma_{\text{in}}+\sigma_{\text{out}}=-\int_0^{\tau/2}\rho_{\text{el}}(x)dx-\int_{\tau/2+d}^{\infty}\rho_{\text{el}}(x)dx \ , \tag{4}$$

where the first and second integrals define σ'_{in} and σ'_{out}, respectively. That is, the induced electrical charge in the solution cancel exactly the electrical field produced by the surface charge on the slit. Only half of the space is considered in Eq. (4), since, by symmetry, the other half is its mirror image.

The conservation of the total charge in classical systems is a well established principle. If constant charge or constant potential boundary conditions are imposed, any reasonable liquids theory should satisfy Eq. (4). From Eq. (1) it can be seen that the concentration profile inside the slit depends on that on the outside and on the thickness of the walls of the plates. Hence, in general, it is reasonable to expect $-\sigma'_{\text{in}}$ and $-\sigma'_{\text{out}}$ *not* to be equal to σ_{in} and σ_{out}, respectively. However, mathematical manipulation of Eqs. (3) and (4) shows that [1,2] for the *constant potential* boundary conditions, in addition to Eq. (4),

$$\sigma_{\text{in}}=-\sigma'_{\text{in}}\equiv-\int_0^{\tau/2}\rho_{\text{el}}(x)dx \ , \tag{5}$$

$$\sigma_{\text{out}}=-\sigma'_{\text{out}}\equiv-\int_{\tau/2+d}^{\infty}\rho_{\text{el}}(x)dx \ . \tag{6}$$

That is, if $\Psi_{\text{in}}=\Psi_{\text{out}}$ a *local electroneutrality condition* (LEC) is satisfied. In this case the fluid inside the slit cancels the electrical field produced on the inside surfaces of the slit, whereas the electrolyte on the outside cancels the field of the outside surfaces of the slit. For the constant charge case *no* proof has been given for a general validity or invalidity of a LEC. Using Eqs. (5) and (6) it can be shown [1,2] that, for the constant potential boundary conditions, the solution to Eq. (1) inside the slit is independent of that in the outside and of the thickness of the walls. Thus, if the surface potential is fixed, the induced surface charge density on the inside surfaces of the slit will depend on the distance between the walls, whereas that on the outside surfaces will be constant and in general $\sigma_{\text{in}}\neq\sigma_{\text{out}}$. On the other hand, if the surface charge is fixed Eq. (4) must be used and the solution to Eq. (1) inside the slit will in general depend on that on the outside of the slit. Hence, the surface potential will be a function of the distance between the walls and the thickness of the walls and in general $\Psi_{\text{in}}\neq\Psi_{\text{out}}$.

In the past, it has been pointed out that for the constant charge case the more general electroneutrality condition Eq. (4) should be used instead of a LEC [1,2], since no proof existed of the validity of a LEC for this important case. Clearly, at least in the limit of $\tau\rightarrow 0$ a LEC can not be satisfied. The validity or invalidity of a LEC, for larger values of τ will depend on a balance between the need of the counterions to cancel the plates' electrical field and their own repulsion. Thus, it is not obvious under which circumstances a LEC will be valid for constant charge boundary conditions. To prove the validity or invalidity of a LEC, a liquid theory as Eq. (1) *must* be solved. This is because, as we show in this paper, the validity of a LEC at constant charge boundary conditions depends on the system's parameters and, hence, no general proof can be given. In the literature the LEC of Eq. (5) has been forced on the confined fluid, while the fluid outside the plates is ignored. That is, in the literature σ_{in} is fixed and the condition of Eq. (5) is arbitrarily forced on the confined liquid, while no condition is imposed on the external surfaces of the slit or the external fluid; in fact they are completely ignored. One can fix σ_{in} and use the LEC for the confined fluid Eq. (5) as boundary conditions in the solution of Eqs. (1) and (3). It will be shown here that this forces the system to accomplish the condition $\Psi_{\text{in}}=\Psi_{\text{out}}$ but, in this case, the surface potential adjusts to a different value for every distance τ between the plates. Let us call these boundary conditions the local electroneutrality (LE) boundary conditions. For these boundary conditions the result of the integral on the right hand side of Eq. (5), say $\sigma'_{\text{in-LE}}$, is equal to σ_{in}, by construction. However, the result of the integral on the right hand side of Eq. (6), say $\sigma'_{\text{out-LE}}$ will be in general a function of τ. We have solved the TPE-HNC-MSA equation for the constant charge, constant potential and LE boundary conditions for several electrolyte and slit parameters. In this paper we show our results for electrolyte and plates parameters that are suitable for comparison with existing [8] GCMC results. In their simulation the authors fixed the charge on two sheets of charge, as a function of τ. However, they also imposed a LEC on the confined fluid. As a result, they in fact did a correct simulation for LE boundary conditions and not for constant charge boundary conditions, as they said they were doing.

III. RESULTS

We solved the TPE-HNC-MSA equation for two charged plates immersed in a RPM electrolyte solution, for constant charge, constant potential, and local electroneutrality boundary conditions. This equation was solved also for the limit case of zero ionic diameter. The concentration profiles and the charge induced in the solution were obtained. The net pressure between the plates as a function of the plates' separation was calculated. We have made calculations for 1:1 and 2:2 electrolytes for various electrolyte's concentrations and plates' surface charges. All the calculations were made for $T=298$ K, $\varepsilon=78.5$, and $a=4.25$ Å. All the results reported here, except those in Fig. 5, which are for a point ion model (PIM) for electrolytes, are for a RPM electrolyte.

We have organized our results in two sections. In Sec. III A, we show results for the charge induced on the electrolyte by the charge slit. We present TPE-HNC-MSA results for constant charge, constant potential, and local electroneutrality boundary conditions. Counterion concentration profiles for the RPM and the PIM are also presented. In Sec. III B, we calculate the net pressure between the plates for these three boundary conditions but our emphasis is on the local electroneutrality boundary conditions, since there are computer simulations results only for this case.

A. Local electroneutrality condition range of validity

In Fig. 2 we show the negative of the charge induced, by the slit, on the fluid, for the LE and constant charge $\sigma_{\text{in}}=\sigma_{\text{out}}$ boundary conditions, as a function of τ. That is, we show the values of the right hand integral of Eqs. (5) and (6). We have denoted these quantities as σ'_{in} and σ'_{out}, for the constant charge case, and $\sigma'_{\text{in-LE}}$ and $\sigma'_{\text{out-LE}}$ for the LE case. The total induced charge on both sides of one plate of the slit and for the two boundary conditions considered here are: $\sigma'_{\text{tot}}=\sigma'_{\text{in}}+\sigma'_{\text{out}}$ and $\sigma'_{\text{tot-LE}}=\sigma'_{\text{in-LE}}+\sigma'_{\text{out-LE}}$. In Fig. 2, the fluid is a 2:2, 0.971 *M* electrolyte and $\sigma_{\text{in}}=\sigma_{\text{out}}=0.272$ C/m^2. As the plates approach each other, for the LE case, $\sigma'_{\text{in-LE}}$ is a constant equal to 0.272 C/m^2, by construction. However, $\sigma'_{\text{out-LE}}$ and $\sigma'_{\text{tot-LE}}$ are non-monotonic functions of τ. On the other hand, for the constant charge case, σ_{in} and σ'_{out} are nonlinear functions of τ, whereas σ'_{tot} is a constant equal to 0.544 C/m^4. This shows that if the charge is fixed on the plates, the LEC will not be satisfied in narrow slits.

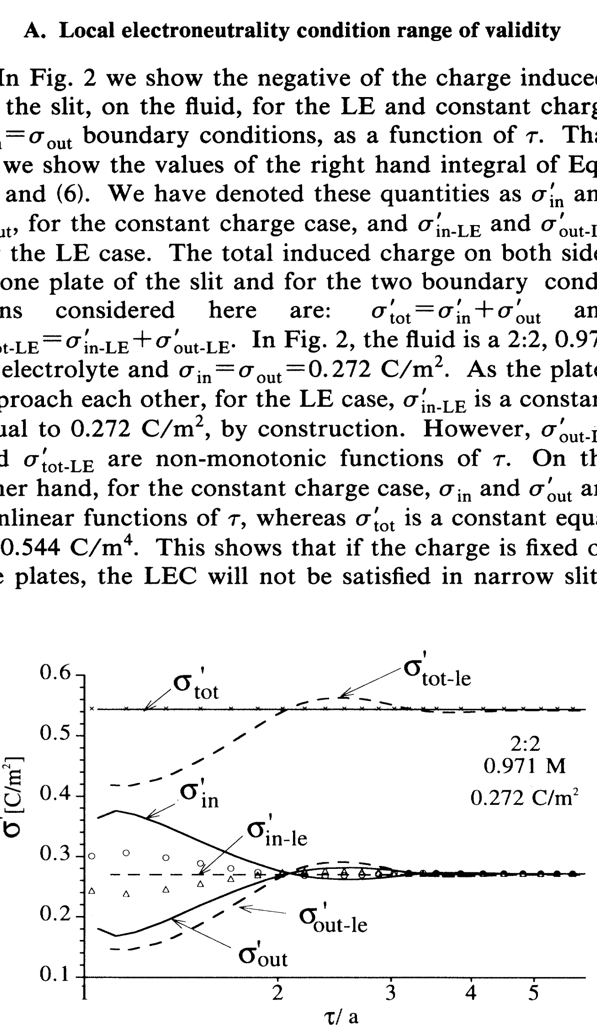

FIG. 2. Charge density induced into a 2:2 restricted primitive model (RPM), symmetrical electrolyte by a charged slit, as a function of the plates' separation τ. The electrolyte's bulk concentration is 0.971 *M* and the surface charge density on the plates is $\sigma_{\text{in}}=\sigma_{\text{out}}=0.272$ C/m^2. σ'_{in} and σ'_{out} are the induced charge in the fluid inside and outside the slit, respectively, for the constant charge boundary conditions and $d=0$. σ'_{tot} is the sum of σ'_{in} and σ'_{out}. $\sigma'_{\text{in-LE}}$ and $\sigma'_{\text{out-LE}}$ are the induced charge in the fluid inside and outside the slit, respectively, for the LE boundary conditions. $\sigma'_{\text{tot-LE}}$ is the sum of $\sigma'_{\text{in-LE}}$ and $\sigma'_{\text{out-LE}}$. a is the ionic diameter. The white dots and triangles are results for σ'_{in} and σ'_{out}, respectively, for $d=a$. The crosses are values of σ'_{tot} for $d=a$.

For the constant charge case the LEC is satisfied for large distances between the plates, compared to the thickness of the EDL. The lower the electrolyte concentration and/or the electrolyte valence and/or the thinner the plates of the slit the larger the distance between the plates at which the LEC begins *not* to be satisfies. As a rule, the thicker the EDL, the larger the value of τ at which the LEC is not satisfied and the larger the deviation of the induced charge, from its limit value at $\tau\rightarrow\infty$. A 2:2, 0.971 *M* electrolyte has a very narrow EDL. Therefore, for these conditions, the effect is noticeably only for small values of τ and d. However, for a, say, 1:1, 0.01 *M* electrolyte this effect is significant for values of τ and d of the order of 100a, i.e., 400 Å. For electrolytes with even thicker EDL's the violation of the LEC shows for values of τ or d up to 40 000 Å. In Fig. 2, we have chosen to plot the curves for $d=0$ and $d=a$, for better showing the violation of the LEC. For these electrolyte parameters, the LEC is approximately satisfied even for very small values of τ if d is equal to 10a or larger, i.e., σ'_{in} and σ'_{out} are approximately equal to 0.272 C/m^2, for every value of τ. We performed calculations for values of d as high as 100a and 10 000a. For $d=100a$ the LEC, for this very short EDL system, is satisfied 99.986%. For $d=10a$, the LEC is satisfied 99.872%. For $d=10\,000a$ the LEC is satisfied 99.999 86%. Clearly, if τ is lower than a the LEC is never valid in this model. If from the LE boundary conditions calculations we get the surface mean electrostatic potential on the inside surfaces of the slit and make this potential equal to that on the outside and use these potentials to feed the TPE-HNC-MSA equation for constant potential boundary conditions, we find exactly the same results as those with the LE boundary conditions. This is of course to be expected since if the LEC is forced in Eq. (5), from Eq. (4), the Eq. (6) is obtained and from Appendix B of Ref. [1], it follows that the surface mean electrostatic potential on both sides of the plate must be equal.

In Fig. 3 we show the induced charge for the constant

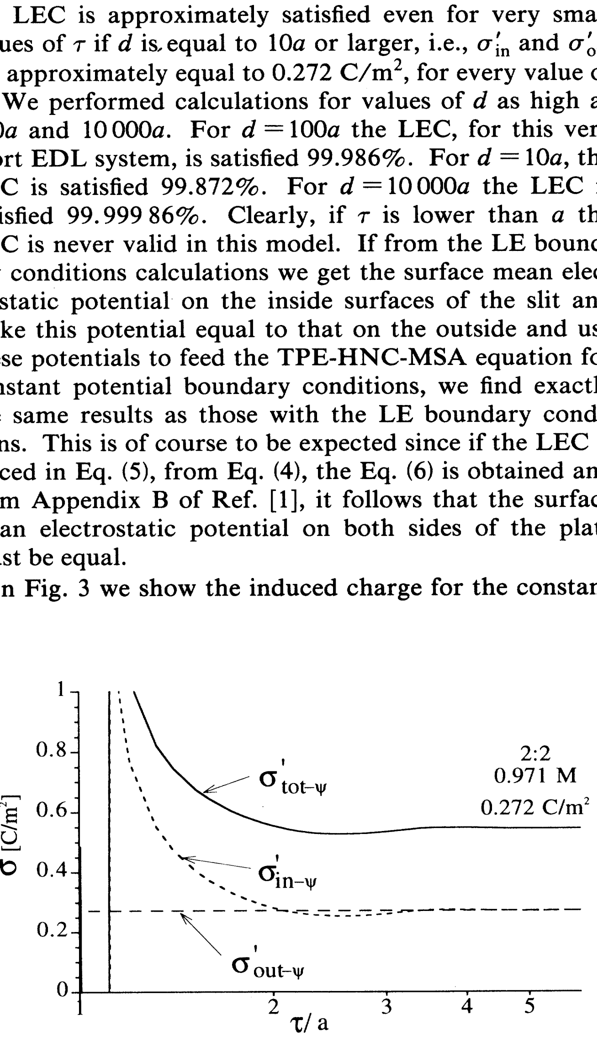

FIG. 3. Charge density induced into a 2:2 RPM symmetrical electrolyte by a charged slit, as a function of the plates' separation τ. $\sigma'_{\text{in-}\psi}$ and $\sigma'_{\text{out-}\psi}$ are the induced charge in the fluid inside and outside the slit, respectively, for the constant potential boundary conditions. $\sigma'_{\text{tot-}\psi}$ is the sum of $\sigma'_{\text{in-}\psi}$ and $\sigma'_{\text{out-}\psi}$. a is the ionic diameter.

potential boundary condition, $\Psi_{\text{in}}=\Psi_{\text{out}}$. The fluid is also a 2:2, 01971 M electrolyte and $\sigma_{\text{in}}=\sigma_{\text{out}}=0.272$ C/m^2 for an infinite separation of the plates. Here, as mentioned above, the surface potential on the plates is kept constant for every plates separation and, hence, the surface charge will be equal to that induced in the liquid. In this case, $\sigma'_{\text{out-}\Psi}$ remains a constant equal to 0.272 C/m^2, but $\sigma'_{\text{in-}\Psi}$ and $\sigma'_{\text{tot-}\Psi}$ are nonmonotonic functions τ. This case, as that of LE, implies a nonconstant Gibbs free energy of the system as a function of the plates' separation, due to changes in the total charge, even though the chemical potential of the salt is a constant.

In Fig. 4 we show the negative of the charge induced, by the slit, on the fluid, for the constant charge $\sigma_{\text{in}}=\sigma_{\text{out}}$, boundary conditions, as a function of τ. The fluid is a 1:1, 0.01 M electrolyte and $\sigma_{\text{in}}=\sigma_{\text{out}}=0.012$ C/m^2. Two main differences with the constant charge results of Fig. 2 can be seen: The LEC is violated up to much longer distances between the plates and σ'_{in} and σ'_{out} are now monotonic. For the 2:2 case σ'_{in} oscillates between higher and lower values of that of σ_{in}, whereas in Fig. 4 σ'_{in} is always lower than σ_{in}. This, of course, implies that for the 1:1 case the confined electrolyte does not cancel the electrical field produced by the inside surfaces of the slit, but for large distances between the plates, and for the 2:2 case the induced field can be higher than that produced by the inside surfaces of the slit. The charge induced in the confined electrolyte can be higher than σ_{in} since, as pointed out before, the induced charge depends on the total charge on the slit and the structure of the confined electrolyte depends on that in the outside of the slit. This shows a nonlinear dependence of the induced field on the ionic valence and the slit's surface charge. In Fig. 4 we have not shown results for PIM. However, we did this calculation and the σ'_{in} and σ'_{out} curves for the PIM are on top of those for the RPM. This is not surprising since for this very low ionic concentration the ionic size effects are not expected to be significant. The distance between the plates at which the LEC begins to be violated increases with lower ionic valence and concentration .

In Fig. 5 we show results for the same conditions to those in Fig. 4, but here we have taken the width of the slit's plates ten times thicker, i.e., $d=10a$. The results shown here are for the PIM. The effect of increasing the value of d is that of decreasing the violation of the LEC.

In Fig. 6 counterion concentration profiles around one of the plates of a charged slit, as a function of the distance to an imaginary plane located at the mid distance between the plates, are shown. The fluid is a 1:1, 0.01 M electrolyte. The plates are one ionic diameter of width and $\sigma_{\text{in}}=\sigma_{\text{out}}=0.012$ C/m^2. These values of the system's parameters corresponded to those of Fig. 4. The distance between the plates τ is (a) $100a$, (b) $10a$, (c) $3a$. In the three figures the curve on the left correspond the confined fluid and that on the right to the fluid outside the slit. As the distance between the plates decreases the counterion concentration near the plate increases. However, the counterion concentration of the confined fluid clearly increases more than that for the fluid outside the slit. At this very low concentration the ionic size should not play a relevant role. Counterion concentration profiles for the PIM have a similar behavior. From Figs. 4–6 it is clear that the violation of the LEC has less than nothing to do with ionic size effects. The violation of the LEC is also *not* a consequence of the fact that for short distances between the plates the integral in Eq. (5) is of shorter range than that in Eq. (6), since, as has been shown in the past [1,2], the LEC is always satisfied for constant potential boundary conditions.

In Fig. 7 counterion concentration profile around one of the plates of a charged slit, as a function of the distance to an imaginary plane located at the mid distance between the plates, are shown. The fluid is a 2:2 0.971 M electrolyte. The plates are zero ionic diameter of width and $\sigma_{\text{in}}=\sigma_{\text{out}}=0.272$ C/m^2. These values of the system's parameters correspond to those for constant charge boundary conditions and $d=0$ of Fig. 2. The distance between the plates τ is (a) $2.52a$, (b) $1.52a$. In the two figures the curve on the left corresponds to the confined fluid and that on the right to the fluid outside the slit.

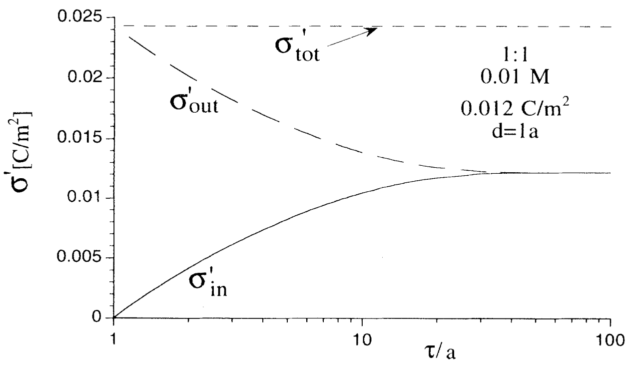

FIG. 4. Charge density induced into a 1:1 RPM symmetrical electrolyte by a charged slit, as a function of the plates' separation τ. σ'_{in} and σ'_{out} are the induced charge in the fluid inside and outside the slit, respectively, for the constant charge boundary conditions and $d=a$. σ'_{tot} is the sum of σ'_{in} and σ'_{out}.

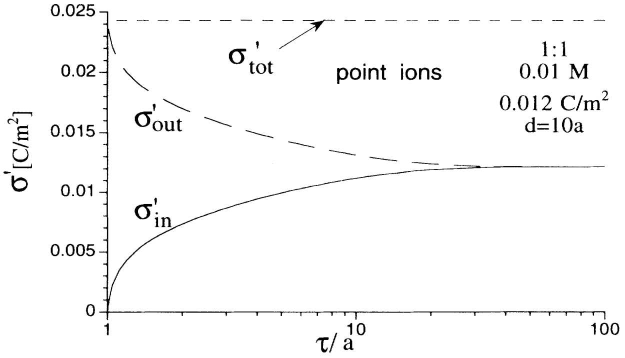

FIG. 5. Charge density induced into a 1:1 point ion symmetrical electrolyte by a charged slit, as a function of the plates' separation τ. σ'_{in} and σ'_{out} are the induced charge in the fluid inside and outside the slit, respectively, for the constant charge boundary conditions and $d=10a$. σ'_{tot} is the sum of σ'_{in} and σ'_{out}.

From Figs. 2 and 7 we see that when $\sigma'_{\rm in}$ is lower than $\sigma_{\rm in}$, i.e., $\sigma'_{\rm out}$ is higher than $\sigma_{\rm out}$, the counterion concentration of the confined fluid is lower than that on the outside Fig. 7(a). However, if $\sigma'_{\rm in}$ is higher than $\sigma_{\rm in}$, i.e,. $\sigma'_{\rm out}$ is lower than $\sigma_{\rm out}$, the counterion concentration of the confined fluid is higher than that on the outside Fig. 7(b).

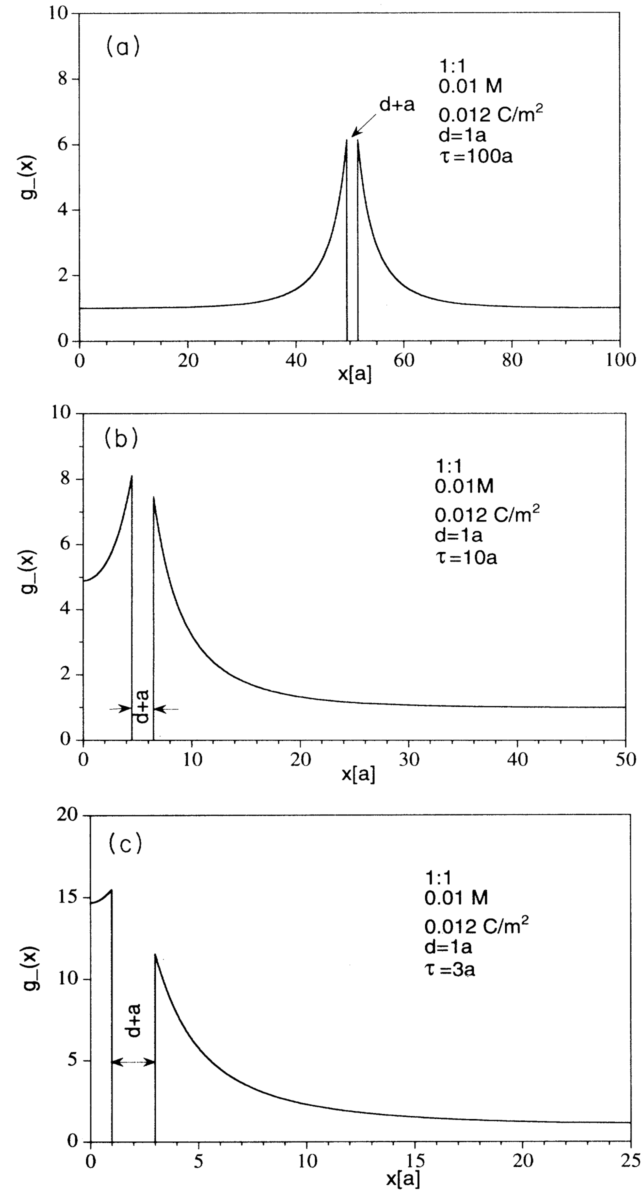

FIG. 6. Counterion concentration profile around one of the plates of a charged slit, as a function of the distance to an imaginary plane located at the mid distance between the plates. The counterion concentration profile around the other plate is, by symmetry, its mirror image. The TPE-HNC-MSA equation was here solved for constant charge boundary conditions. The fluid is a 1:1, 0.1 *M* electrolyte. The plates are one ionic diameter of width and $\sigma_{\rm in}=\sigma_{\rm out}=0.012$ C/m². The distance between the plates τ is (a) $100a$, (b) $10a$, (c) $3a$. In the three figures the curve on the left corresponds to the confined fluid and that on the right to the fluid outside the slit.

B. Plate-plate interaction force

The force between two plates immersed into an electrolyte solution is a quantity of interest in the study of complex liquids. The general expression for the calculation of this force is [1]

$$P(\tau)=\left\{kT\rho_s(\tau;t-a/2)-\frac{2\pi}{\varepsilon}\left[\int_{a/2}^{t}\rho_{\rm el}(\tau;y)dy\right]^2\right\}-\left\{kT\rho_s(\tau;t+d+a)-\frac{2\pi}{\varepsilon}\left[\int_{t+d+a}^{\infty}\rho_{\rm el}(\tau;y)dy\right]^2\right\}, \quad (7)$$

where t is the distance from the center of the slit to the surface of the right hand side plate (see Fig. 1), $\rho_{\rm el}(\tau;y)$ is the charge profile, as defined in Sec. II, for a distance between the plates of τ, and

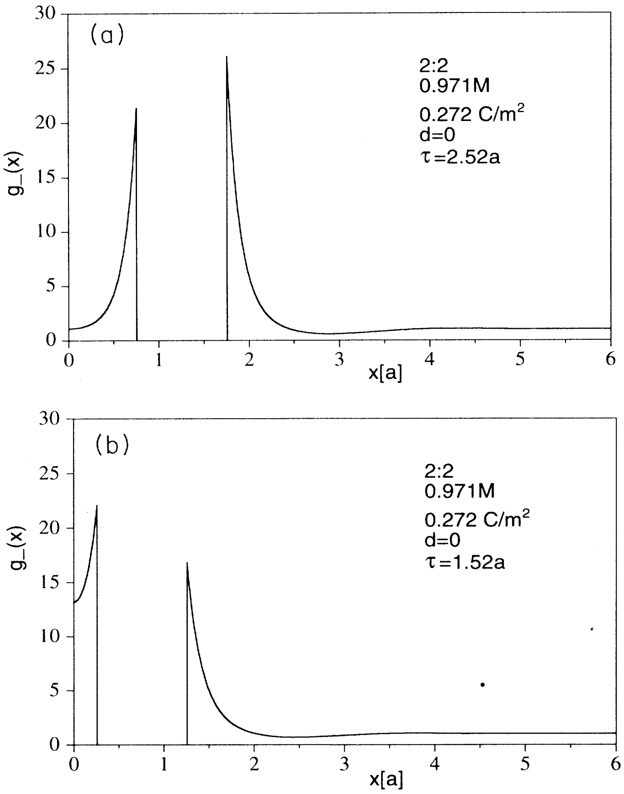

FIG. 7. Counterion concentration profile around one of the plates of a charged slit, as a function of the distance to an imaginary plane located at the mid distance between the plates. The counterion concentration profile around the other plate is, by symmetry, its mirror image. The TPE-HNC-MSA equation was solved here for constant charge boundary conditions. The fluid is a 2:2, 0.971 *M* electrolyte. The plates are zero ionic diameter of width and $\sigma_{\rm in}=\sigma_{\rm out}=0.272$ C/m². The distance between the plates τ is (a) $2.52a$, (b) $1.52a$. In the two figures the curve on the left corresponds to the confined fluid and that on the right to the fluid outside the slit.

$$\rho_s(\tau;t-a/2)=\sum_{m=1}^{2}\rho_m g_{am}(\tau;t-a/2)\ , \tag{8}$$

such that the reduced concentration profile is evaluated for $x=t-a/2$, i.e., at contact with the inside surface of the slit and

$$\rho_s(\tau;t+d+a)=\sum_{m=1}^{2}\rho_m g_{am}(\tau;t+d+a)\ , \tag{9}$$

such that the reduced concentration profile is evaluated at contact with the outside surface of the slit. Equation (7) takes into account the fact that a LEC not necessarily is satisfied.

In Sec. III A we showed that the LEC is not satisfied for constant charge boundary conditions. However, if constant potential boundary conditions are imposed to the slit the LEC will always be satisfied [1,2]. As pointed out in the Introduction, in the literature, calculations have been made for special boundary conditions in which they fix the charge on the inside surfaces of the slit, force the LEC to be valid and simply ignore the fluid outside. We have named these boundary conditions as local electroneutrality (LE) boundary conditions. These boundary conditions have been mistakenly taken in the literature is our constant charge boundary conditions. In complex fluids, in particular for lyophobic colloids, it is more realistic to assume our constant charge boundary conditions than LE boundary conditions. Since for whatever reason all the MC simulations [3–8], integral equation results [9–15], and density functionals results [16–19] we know are for LE boundary conditions, in this section we calculate the force for LE boundary conditions and compare our results with those of GCMC simulations [8] to show the accuracy of our results. In addition, we show the plate-plate force for constant charge and constant potential boundary conditions for comparison.

As pointed out above, the GCMC simulation of Valleau, Ivkov, and Torrie [8] was made, for two sheets of charge, with LE boundary conditions. In Fig. 8 we compare, in principle, the exact pressure on the plates, in units of ρkT, reported by Valleau, Ivkov, and Torrie with that obtained form the TPE-HNC-MSA for the three boundary conditions analyzed above, i.e., constant charge, LE, and constant potential. The fluid is a 2:2, 0.971 M symmetrical electrolyte. The plates are zero ionic diameter of width and $\sigma_{\text{in}}=\sigma_{\text{out}}=0.272$ C/m^2. It is seen as a very good agreement of the LE curve with the GCMC data. This result tests the theory. The constant charge case exaggerates the attractive minimum and the constant potential case exaggerates this minimum considerably more. The dash curve is the TPE-HNC-MSA calculation for the constant charge case, for $d=0$ (sheets of charge). The case for $d=10a$ (i.e., $d=42$ Å) is on top on the constant potential case TPE-HNC-MSA curve (i.e., the solid line) and it is not explicitly shown. It is to be expected that for sufficiently large values of d the constant charge pressure agrees with the LE boundary conditions pressure, since for large values of d the constant charge calculations satisfy the LEC, as shown in Fig. 2. Thus, for $d=10a$ the TPE-HNC-MSA constant charge curve also has *a very good agreement* with the GCMC results. The role of the parameter d increases with increasing thickness of the EDL's associated to the plates of the slit. In Fig. 8(b), we present the LE and constant charge results in a scale suitable to see the accuracy of our theory for small values of the pressure. The white dots are GCMC results also obtained in Ref. [8]. We have singled them out because if they are multiplied by -1 they have good agreement with our results.

In Fig. 9 we show the interaction force per unit area between two charged plates immersed into a 2:2, 0.971 M symmetrical electrolyte, as a function of the distance between the plates. The plates are zero ionic diameter of width and $\sigma_{\text{in}}=\sigma_{\text{out}}=0.091$ C/m^2. The TPE-HNC-MSA pressure for constant charge and LE boundary conditions are compared to GCMC calculations [8]. The constant charge pressure is more negative, around $\tau=2a$, then the LE pressure. This behavior is similar to that seen in Fig. 8. For this lower surface charge density the absolute value of the pressure (negative or positive) is lower. The agreement between the constant charge and LE pressure

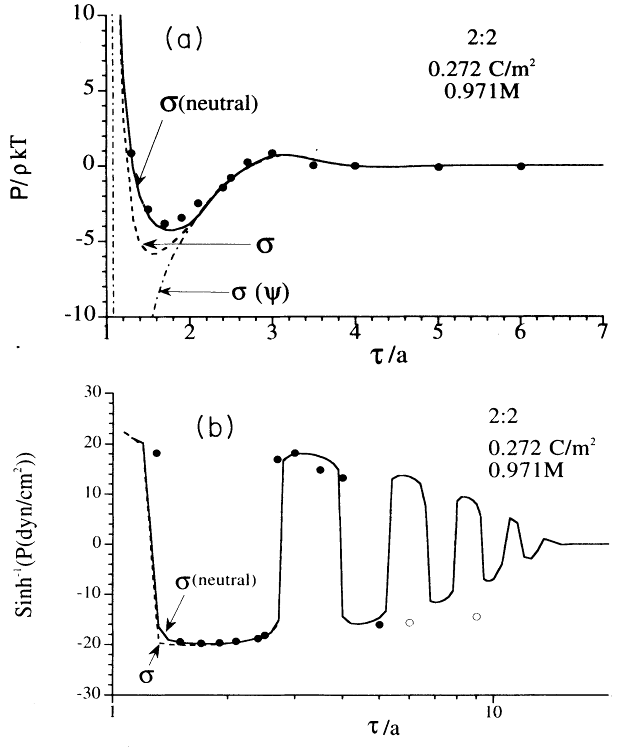

FIG. 8. Interaction force per unit area P between two charged plates immersed into a 2:2, 0.971 M symmetrical electrolyte, as a function of the distance between the plates. The plates are zero ionic diameter of width and $\sigma_{\text{in}}=\sigma_{\text{out}}=0.272$ C/m^2. ρ is the total bulk electrolyte concentration. The black and the white dots are GCMC results [8]. The solid, dashed, and dot-dashed curves are the TPE-HNC-MSA results for LE, constant charge, and constant potential boundary conditions on the plates, respectively. In (a) linear scales are used for the pressure and the distance between the plates. In (b) nonlinear scales are used and no results for the constant potential boundary conditions are shown.

curves is similar to that in Fig. 8. For large values of *d*, the constant charge pressure becomes higher than the LE pressure. The agreement of our results with the GCMC data is not as good as that seen in Fig. 8. This is puzzling since a higher surface charge is a more demanding parameter for the TPE-HNC-MSA theory. In Fig. 9(b) the pressure is shown in a nonlinear scale. The white GCMC dots are from the same source as the black ones. We, as in Fig. 8, have singled them out to point out that if they are multiplied by -1 they fall on the TPE-HNC-MSA curves. The sequence of the black dots seems to indicate that the white dots may have a sign misprint.

For constant potential boundary conditions Eq. (1) can be solved for the fluid inside independently of its solution for the fluid outside. This is not possible for the constant charge boundary conditions, i.e., Eq. (1) must also be solved simultaneously for the fluid inside and outside the slit. This is a much more demanding calculation. For the LE boundary conditions, Eq. (1) must be solved simultaneously for the fluid inside and outside the slit. The net pressure is obtained by subtracting the pressure on the surface of the plates by the outside fluid from that on the inside. In the literature, the net pressure is found by calculating the pressure on the inside surface of the plates of the slit and then subtracting that pressure when the plates are infinitely apart. It is interesting that in our LE calculation the induced charge on the fluid outside adjust to give the *net* pressure as calculated by Valleau. If in our constant potential program we fix the surface potential such that the induced charge on the fluid is equal to that of Valleau and with this same potential and program we calculate the pressure for an infinitely wide slit we find the same induced charge on the fluid and pressure on the walls as that obtained with our LE program. The net pressure obtained in this way is equal to that of the LE program and Valleau. Therefore, for the net pressure quantity one can just ignore the fluid outside and calculate the net pressure by subtracting the pressure at infinite plate's separation. However, if the system is, for example, a vesicle, the charge induced on the fluid outside will be very different to that of a vesicle of infinite radius.

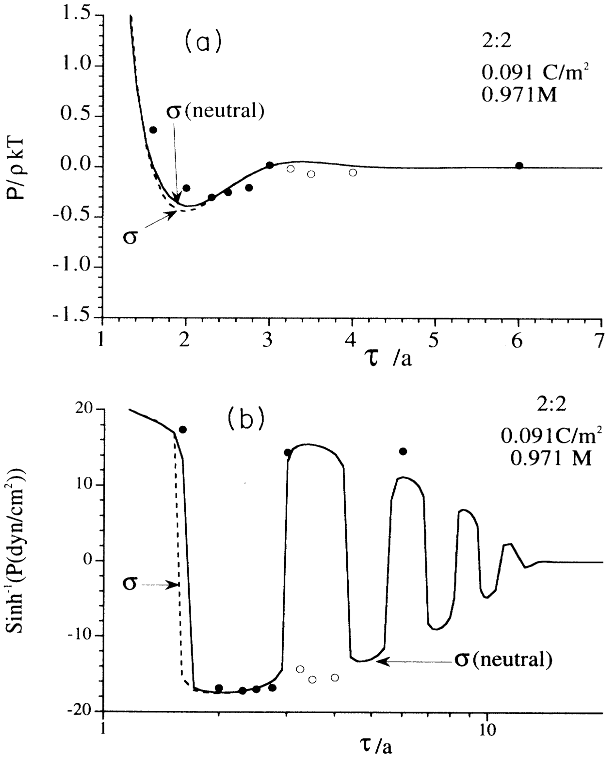

FIG. 9. Interaction force per unit area *P* between two charged plates immersed into a 2:2, 0.971 *M* symmetrical electrolyte, as a function of the distance between the plates. The plates are zero ionic diameter of width and $\sigma_{\text{in}}=\sigma_{\text{out}}=0.091$ C/m^2. ρ is the total bulk electrolyte concentration. The black and the white dots are GCMC results [8]. The solid, dashed, and dot-dashed curves are the TPE-HNC-MSA results for LE, constant charge, and constant potential boundary conditions on the plates, respectively. In (a) linear scales are used for the pressure and the distance between the plates. In (b) nonlinear scales are used.

In Fig. 10 we show the interaction force per unit area between two charged plates immersed into a 1:1, 0.495 *M* symmetrical electrolyte, as a function of the distance between the plates. The plates have a surface charge density $\sigma_{\text{in}}=\sigma_{\text{out}}=0.227$ C/m^2. The TPE-HNC-MSA pressure for LE boundary conditions are compared to anisotropic hypernetted chain (AHNC) equation results [10] and a GCMC point [8]. Professor Valleau and coworkers obtained this GCMC point to compare with the AHNC results of Professors Kjellander and Marcelja. In their paper Valleua, Ivkov, and Torrie did this calculation for a distance between the plates of 8.5 Å and mistakenly compared it to the AHNC pressure for $\tau-a=8.5$ Å. This leads them to say in their paper that the AHNC equation had an excellent agreement with the GCMC results. This was an unfortunate error [28].

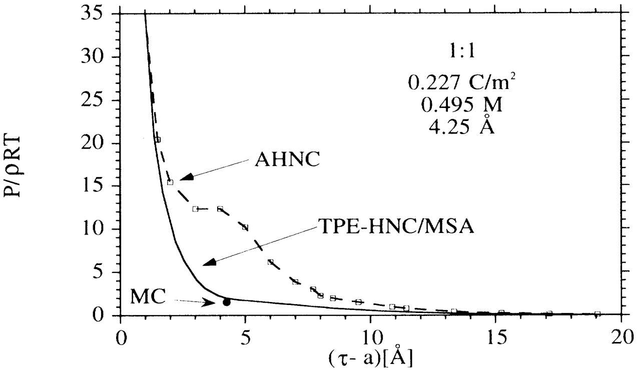

FIG. 10. Interaction force per unit area *P* between two charged plates immersed into a 1:1, 0.495 *M* symmetrical electrolyte, as a function of the distance between the plates. The plates have a surface charge density $\sigma_{\text{in}}=\sigma_{\text{out}}=0.227$ C/m^2. ρ is the total bulk electrolyte concentration. The black dot is a GCMC result [8]. The solid curve is the TPE-HNC-MSA results for LE boundary conditions. The dash–white squares curve are anisotropic hypernetted chain (AHNC) equation results from Fig. 4 of Ref. [10].

From Fig. 10 it is clear that the AHNC result is very far away from the GCMC data and the TPE-HNC-MSA result. On the other hand, in view of Figs. 8 and 9, it is not surprising that we find a good agreement of this GCMC point with the TPE-HNC-MSA result. One point does not prove that the AHNC result is wrong. However, the qualitative behavior of the AHNC pressure curve is in total disagreement with the GCMC and TPE-HNC-MSA results shown in Figs. 8 and 10. The hump shown by the AHNC equation is probably a feature of the theory [29].

IV. CONCLUSIONS

When two charged plates are immersed into a electrolyte solution, the fluid around them polarizes. The general electroneutrality condition establishes that: the charge on the plates plus the induced charge in the fluid gives a net zero charge. This general statement is corroborated by our TPE-HNC-MSA calculations of this system, under several boundary conditions. However, in the literature it has often been assumed a *local electroneutrality condition* (LEC) for the fluid confined by the slit, while the fluid outside is ignored. The general electroneutrality condition does not invalidate, in principle, the LEC. In the past [1,2], a LEC was shown to be valid for constant potential boundary conditions, whereas no proof of general validity or invalidity of the LEC was given for constant charge boundary conditions. In this paper we showed, by solving the TPE-HNC-MSA theory, that if the charge on the plates is fixed, for short distances between the plates, the LEC is violated. The total charge of the system is a constant independent of the distance between the plates. If the electrostatic potential on the plates is fixed the LEC is satisfied, but the total charge is a function of the distance between the plates. If the surface charge is fixed only on the inner surfaces of the slit and the LEC is forced on the liquid between the plates, the LEC for the confined liquid is obviously satisfied since it is used as a boundary condition. However, the LEC is satisfied at the expenses of *no* conservation of the total charge and Gibbs free energy of the system, as a function of the distance between the plates. For sufficiently large values of τ or d the TPE-HNC-MSA force between the plates, obtained with the constant charge boundary conditions, becomes equal to that from the TPE-HNC-MSA solved with the LE boundary conditions, since for large values of τ or d the LEC is satisfied, and these two have a very good agreement with GCMC simulations obtained with LE boundary conditions. It has been said that the AHNC equation is the best theory for inhomogeneous fluids; the results presented here do not seem to support this statement. These findings could be relevant for some biological and complex liquids systems.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of CONACYT, Ref. 3163-E9307, México, and CONICIT, S1-2503, Fundacite Mérida, CDHT, Venezuela.

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