## **Charge Separation in Confined Charged Fluids**

Jiang Yu,<sup>1</sup> Léo Degrève,<sup>2</sup> and Marcelo Lozada-Cassou<sup>1</sup>

<sup>1</sup>Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-534, 09340 México, D.F., Mexico

<sup>2</sup>Faculdade de Filosofia, Ciências e Letras, Universidade de São Paulo, Ribeirão Preto, São Paulo, Brasil

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A charge segregation phase is found in a charged fluid confined by a charged spherical pore: The negative ions are completely separated from a spherical core comprised of only positive ions. Within the segregation regime, there is a region for which the pressure decreases with increasing fluid confinement. [S0031-9007(97)04362-7]

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The structure of ionic solutions near the inside and outside surfaces of spherical cavities is relevant to some biological and complex fluid phenomena [1,2]. The structure of fluids inside micropores and near charged planar and curved surfaces have attracted wide attention [2–13]. Some interesting features of inhomogeneous charged fluids have been uncovered theoretically and confirmed by Monte Carlo (MC) simulations [8] and some experiments [5]. Particularly, it has been predicted [3] that a local electroneutrality condition (LEC) is, in general, not satisfied and that charged fluids at both sides of a charged wall are correlated under certain circumstances [13]. These results may be of some relevance for confined charged fluid systems. Apparently these effects have not been taken into account in previous studies [12,13].

The inhomogeneous fluids inside a spherical shell (SS) have been studied extensively in recent years [2,4,6,7]. However, the violation of the LEC in spherical pores or SS (a spherical pore is a SS of infinite thickness) and/or the correlation between the fluids separated by a SS have not been considered in the past. Here we give a theoretical description of a (SS) model immersed in an electrolyte solution, where no LEC is imposed and the correlation between the fluids internal and external to the shell are taken into account: We find a segregation of charge in the confined, inhomogeneous, charged fluid. Within this segregation phase an interesting state characterized by  $\partial p/\partial \ln v > 0$  is found, where p is the confined liquid pressure and v is the pore's volume. It is well known that a negative compressibility is unphysical in homogeneous fluid systems.

Our model system consists of a hard, charged SS with finite shell thickness, immersed in an ionic solution. We denote the radius of the inner surface of the SS by R, and the shell thickness by d. The SS could mimic the membrane of a vesicle or a micelle. A widely used model for the electrolyte is the restricted primitive model (RPM) [13].

The hypernetted chain/mean spherical (HNC/MSA) theory for a hard, charged SS immersed in a RPM electrolyte can be readily derived from the homogeneous OrnsteinZernike (OZ) equation, by applying the so-called direct method (DM) [9],

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

where  $dv_3$  is the volume differential in a spherical coordinates system, with its origin at the center of the sphere defined by the shell.  $\rho_m$  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;  $\rho_i g_{\alpha i}(r)$  is the local concentration of ions of species *i*, at a distance r from the coordinates origin;  $h_{\alpha m}(t)$ , defined as  $h_{\alpha m}(t) \equiv g_{\alpha m}(t) - 1$ , is the total correlation function;  $\beta \equiv 1/k_B T$ , where  $k_B$  is the Boltzmann constant and T is the system temperature;  $u_{\alpha i}(r)$  is the direct interaction potential between an ion of species *i* and the SS, represented by the subindex  $\alpha$ . The shell-ion interaction is described by a hard-core term,  $u_{\alpha i}^{*}(r)$ , plus an electrostatic part,  $u_{\alpha i}^{el}(r)$ . The hard sphere-hard shell potential takes into account the fact that the ions cannot penetrate or deform the shell. By applying Gauss's law the electrostatic potential between the SS and ions is found to be

$$u_{\alpha i}^{\text{el}}(r) = \begin{cases} 4\pi e z_i [(R + d)^2 \sigma_{\text{out}} + R^2 \sigma_{\text{in}}]/\varepsilon r, \\ r \ge R + d; \\ 4\pi e z_i [(R + d) \sigma_{\text{out}} + R \sigma_{\text{in}}]/\varepsilon, \\ r < R, \end{cases}$$
(2)

where  $\sigma_{\rm in}$  and  $\sigma_{\rm out}$  are the charge densities on the inside and outside surfaces of the shell, respectively. The presence of the charged shell in the electrolyte will result in an induction of charge in the solution inside and outside the pore. The induced charge density on the inner and outer liquids are  $\sigma'_{\rm in} = -(1/R^2) \int_0^{R-a/2} t^2 \rho_{\rm el}(R-a/2-t) dt$ and  $\sigma'_{\rm out} = -[1/(R+d)^2] \int_{R+d+a/2}^{R} t^2 \rho_{\rm el}(t-R-d-a/2) dt$ , respectively, where  $\rho_{\rm el}(r) = \sum_{m=1}^n e z_m \rho_m h_{\alpha m(r)}$ is the induced charge profile. The LEC is satisfied if  $\sigma_{\rm in} = \sigma'_{\rm in}$  and  $\sigma_{\rm out} = \sigma'_{\rm out}$ . The total electroneutrality condition (TEC) is given by  $R^2 \sigma_{\rm in} + (R+d)^2 \sigma_{\rm out} = R^2 \sigma'_{\rm in} + (R+d)^2 \sigma'_{\rm out}$ .

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The pressure on the confined liquid can be found to be

$$p(R) = k_B T [\rho_{\alpha s}(R + d + a/2) - \rho_{\alpha s}(R - a/2)] + \frac{2\pi}{\varepsilon} [(\sigma'_{out})^2 - (\sigma'_{in})^2] + \frac{\varepsilon}{4\pi} \left[ \frac{1}{(R + d + a/2)^2} \int_{R+d+a/2}^{\infty} r E^2(r) dr + \frac{1}{(R - a/2)^2} \int_{0}^{R-a/2} r E^2(r) dr \right],$$
(3)

where  $\rho_{\alpha s}(r) \equiv \sum_{n=1}^{2} \rho_n g_{\alpha n}(r)$  and E(r) is the local electrical field, obtained from  $\rho_{el}(r)$ . We have numerically solved the HNC/MSA equations under the condition of constant surface charge density. From Eq. (1) it follows that the ionic concentration profiles inside the SS are coupled with those outside it, since the integral is over all the space [3]. If the LEC is violated, the net charge inside the SS will produce an electrical field, which will affect the structure of the outside charged fluid. The violation of the LEC is due to the combination of two effects: the confinement of the fluid [3,12] and the correlation between the separated fluids [13]. When the modified Poisson-Boltzmann theory is applied to a confined, point ion model electrolyte a violation of the LEC is also present [12], indicating that the ionic size is not a crucial factor for the breakdown of the LEC.

We have calculated the radial distribution functions  $g_{\alpha i}(r)$ , the pressure on the confined liquid, the mean electrostatic potential, and the induced charge for a 2:2, 0.971 M RPM model electrolyte at T = 298 K, and  $\varepsilon = 78.5$ . The diameter of the ion is taken to be a = 4.25 Å. The surface charge density on the SS is  $\sigma_{in} = \sigma_{out} = 0.272 \text{ C/m}^2$ . In Fig. 1 we show the HNC/MSA pressure on the confined liquid as a function of the SS are considered: d = a, 10*a*, and 200*a*. The d = 200a curve is, for plotting purposes, on the d = 10a curve; hence, it



FIG. 1. Pressure on the confined liquid as a function of the SS radius, in logarithmic scale. The fluid is a 2:2, 0.971 M RPM electrolyte. The solid and dashed curves are for d = a and d = 10a, respectively. The lower inset is an enlargement of the d = a curve. The inset with the black dots are the MC data, for an approximate bulk concentration of 0.960, while the solid line there is its interpolation.  $\sigma_{in} = \sigma_{out} = 0.272 \text{ C/m}^2$ .

is not plotted. A relevant feature here is the anomalous decrease in pressure, as *R* decreases, around R = 3.8a. These curves closely resemble the liquid-vapor phase transition (LVPT). In the LVPT, the van der Waals (VW) pressure prediction inside the spinodal curve is unphysical. In Fig. 1 we also show Monte Carlo results for the pressure. We will discuss them later.

In Fig. 2, we show the concentration profiles for counterions and coions. For large values of R, inside and outside the SS, we see a local charge oscillation induced by the fixed surface charge on the SS, a property typical of inhomogeneous divalent electrolytes [3,8,13]. Charge oscillation occurs due to a combination of ionic size, concentration, and valence, and the surface charge. At R =3.8a/2, we find that in addition to a layer of only counterions next to the inner surface of the SS, there is a central core formed only by coions. The concentration of the counterions next to the inner surface of the SS is of the same order as that of the coions in the center of the SS. Since the counterions and coions are completely separated and located in different regions, a phase transition from the mixture state to a segregation state occurs in the confined fluid system inside the spherical pore. This segregation phase results from the confinement, and does not depend on the shell thickness in the sense that when the shell thickness is increased, the segregation phase does not disappear. Nevertheless, the correlation between the fluids at both sides of the shell affects the magnitude of the pressure curve and the ionic concentration profiles. The appearance of the coion core is somewhat puzzling, because the formation of such a structure generally requires more energy. This might, in principle, be similar to the condensation transition where the likely charged particles are bounded in a way such that the whole system is in its lowest-energy state. As we further decrease R, the concentration of the coions in the central core decreases until all coions are rejected out of the pore. The ionic concentration profiles outside of the SS are not qualitatively modified as R changes, although quantitative changes are present: This shows that in spite of the fact that  $\sigma_{in} = \sigma_{out}$ a correlation between the liquids inside and outside the SS is present [13], due to an asymmetry in charge produced by the violation of the LEC inside the SS. For values of R larger than that where a "coexistence curve" (defined by a Maxwell equal-area construction; see lower inset in Fig. 1) could be present, a typical charge oscillation, as that shown for R = 6(a/2) in Fig. 2, is observed. For value of R smaller than that where the left branch of this coexistence curve would be present, no positive ions are found inside the SS: A typical concentration



FIG. 2. Counterion and coion concentration profiles inside and outside a charged SS, as a function of the distance to the geometrical center of the SS. Three different values of the SS radius are considered. The left profiles are inside the SS, whereas the outside profiles are at the right. The center of the SS is at r = 0. The thickness of the shell is d = a. The fluid is a 2:2, 0.971 M RPM electrolyte.  $\sigma_{in} = \sigma_{out} = 0.272 \text{ C/m}^2$ . The solid and dashed curves are the HNC/MSA counterion and coion concentration profiles, respectively.

profile would be that shown in Fig. 2, for R = 2.56(a/2). Inside this coexistence curve two *nonuniform* phases coexist: A core formed *only* of coions and a shell of *only* counterions, next to the inside surface of the SS. The transit from larger to shorter SS radius, inside this coexistence curve, is characterized by a continuous increase of the coions core to a maximum, for the SS radius corresponding to the inflection point of the pressure curve in the  $(\partial p/\partial \ln v) > 0$  region, to then continuously decrease until no more coions are inside the SS.

Although inside the LVPT spinodal curve (defined by the points of infinite compressibility) the VW pressure prediction is unphysical for homogeneous systems, our pressure curve and concentration profiles are real. To show this we have performed canonical Monte Carlo simulations for our model. In the MC calculation we, necessarily, imposed the TEC, but *did not* impose a LEC. The use of the standard Metropolis Monte Carlo algorithm for our system is justified since, clearly, the system can be divided into two or more subsystems in order to check the acceptance of a change in position which can occur in the same subsystem or between different subsystems. The canonical MC simulation is equivalent to a particle destruction followed by a creation; i.e., the energies of two configurations are compared. Hard uncharged walls were located at r = RM. Since  $\kappa(RM - R - d) \approx 27$ , no consequence on the diffuse layer structures was detected due to the adsorption or desorption of the electrolytes on the simulation wall.  $\kappa^2 \equiv (4\pi\beta e^2/\epsilon)\sum_{n=1}^2 \rho_m z_m^2$  and  $\kappa^{-1}$  (the Debye radius) is a measure of the range of penetration of the effective electrical field, induced by the SS, on the charged fluid around the SS [14]. The bulk concentration of the electrolyte was adjusted by means of the constant number

of ions. The first 1000 simulation cycles were discarded and 5000 complete cycles were used to obtain the final data. Figures 3 and 4 show a comparison of the MC simulation with our theory: While quantitative differences are present, there is a very good qualitative agreement. Figure 4, inside the transition region, clearly shows the charge separation. Figures 3 and 4 show results for an ionic solution with slightly different concentrations from that in Fig. 1: The experimental concentration is obtained a posteriori, as a consequence of the predetermined number of ions, surface charge densities, and the size of the SS. The determination of the number of ions was made by attempting the desired concentration. All other parameters, however, are equal to those for Fig. 1. For very small values of r, the volume differential used to calculate the number concentration of ions goes to zero. Therefore, no concentration profile is reported for r < 0.1(a/2). We have calculated the MC pressure as a function of R, and we find the same qualitative behavior as that shown by the HNC/MSA theory (see Fig. 1): We find a region of  $\partial p / \partial \ln v > 0$ and the values of R for which  $\partial p / \partial \ln v = 0$  closely correspond to those from the theory. The MC curve, however, is higher than the HNC/MSA curve. This is due, in part, to a HNC/MSA underestimation of  $\rho_{\alpha s}(R - a/2)$  and an overestimation of  $\rho_{\alpha s}(R + d + a/2)$  (see Figs. 3 and 4).

In Fig. 5 we show the deviation from the LEC, as a function of the SS radius, for the d = a case. The deviation from the LEC is given by  $\Delta \sigma_{in} = [R^2/(R + d)^2] (\sigma'_{in} - \sigma_{in})$  and  $\Delta \sigma_{out} = \sigma'_{out} - \sigma_{out}$ . The deviation oscillates with the radius and intersects the zero line at  $R = R_c$ , where  $R_c = 2.56(a/2)$ , at which the local electroneutrality is restored. At  $R \rightarrow 0$  and  $R \rightarrow \infty$  we recover the spherical electrode model [15] and one plate model [13], respectively. The correlation between the separated fluids can change the magnitude of the induced charge, but has no influence on the oscillatory behavior: At  $R = R_c$ ,



FIG. 3. As in Fig. 2, but R = 6.2(a/2). The fluid is a 2:2, 1.137 M RPM electrolyte. The lines have the same meaning as in Fig. 2. The black and white dots are the MC counterion and coion concentration profiles, respectively.



FIG. 4. As in Fig. 3, but R = 3.8(a/2). The fluid is a 2:2, 0.941 M RPM electrolyte. The lines and dots have the same meaning as in Fig. 3. The value of R, for the MC data is 3.7828 ionic radius.

the local electroneutrality is reestablished and the electrical field across the shell vanishes, indicating that there is no Coulomb-like long-range interaction between the charged fluids separated by the shell. For  $R \approx 3.8(a/2)$ , we are on the inflection point of both, the LEC deviation curves and the pressure curve (for d = a). Clearly, the violation of the LEC is related to the observed charge separation.

We found a phase transition from a mixed charge state to a segregation one in charged fluids, confined in a spherical pore. A segregation phase is also observed in cylindrical pores [16] when a LEC is *not* imposed [10]. The charge separation is found for divalent electrolytes, in strongly confined geometries, such as in cylindrical and spherical pores, with high surface charge densities. We find that the segregation phase is not present for a 1:1, 0.01 M electrolyte in spherical pores, or for any type of electrolyte in



FIG. 5. Deviation from the LEC as a function of the SS radius, for the d = a case. The fluid is a 2:2, 0.971 M RPM electrolyte.  $\sigma_{in} = \sigma_{out} = 0.272 \text{ C/m}^2$ . The solid and dashed curves are the HNC/MSA deviations from the LEC inside and outside the SS, respectively.

slitlike pores [12]. This suggests that the phase transition is regulated by the plasma parameter [14]. The appearance of the segregation phase is a result of the correlation between the separated fluids and a violation of the LEC [3,13], in strongly confined charged fluids. In spite of the vast literature on fluids confined to a spherical cavity, such phenomenon has not been observed. In those works, however, a LEC is imposed, and no correlation between the liquids inside and outside the SS is considered. While a spinodal curve has been found in the past for homogeneous electrolyte solutions [17], the coexistent phases there are ion-pairing and mixed independent ions, and a negative compressibility region is unphysical. In our inhomogeneous system, the SS electrical field allows a stable region of negative compressibility and an interface between positive and negative ions as the coexisting phases: Nonuniform concentration profiles manifest themselves in the local thermodynamical properties. The pressure as a function of the specific volume also shows a region of negative compressibility. We find it interesting that a region of negative compressibility for confined fluids has been recently reported [18]. A phase separation similar to that reported here will probably be present in mixtures of confined Lennard-Jones fluids.

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