The effect of entropy on macroions adsorption

Felipe Jiménez-Ángeles$^{1,2}$ and Marcelo Lozada-Cassou$^1$

$^1$Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo,
Lázaro Cárdenas 152, 07730 México, D. F., México

$^2$Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-334, 09340 D.F. México

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We study macroion adsorption on planar surfaces, through a simple model. The importance of entropy in the interfacial phenomena is stressed. Our results are in qualitative agreement with available computer simulations and experimental results on charge reversal and self-assembling at interfaces.

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The physics of macroions adsorption at charged interfaces is subject of recent theoretical and experimental studies because its potential technological applications. It is known that in the neighborhood of a charged surface, low-concentrated solutions of monovalent ions produce an exponentially decaying charge distribution which is well described by Poisson-Boltzmann equation. However, adsorption of multivalent ions displays important deviations from the Poisson-Boltzmann picture and there is not yet a fully accepted theory which well accounts for this situation. In inhomogeneous charged fluids, charge reversal (CR) and charge inversion (CI) have been reported as mechanisms with which systems minimize free energy. CR is the overcompensation of the surface’s charge by a contiguous layer of oppositely charged ions from the fluid. Because of electrostatic equilibrium, next to the CR layer, a second layer of ions (with same charge sign as that of the surface) is formed, producing a CI. In molecular engineering, CR and CI are basic mechanisms for self-assembling polyelectrolyte layers on a charged substrate, reverse mobility experiments, self-assembled DNA-lipid membrane complexes, anomalous macroions adsorption on a Langmuir film, and novel colloids stabilization mechanisms.

Although CR was reported since the early 80’s and some advances in its understanding have been done, the mechanism has not been completely understood. Some authors recognized the relevance of electrostatic and ionic size correlations in CR. In particular, the unsymmetrical size effects (between small coions and counterions) has been considered by Greberg and Kjellander. Their analysis of CR and CI is based on mechanic arguments and is basically correct, although incomplete: the role of the ionic concentration, entropy and charge asymmetry is not discussed, which are not minor effects, as we will see. Recently CR by macroions of an oppositely charged surface was considered by Shklovskii et al. They assert in proposing that, when macroions overseer a charged surface, these macroions are highly ordered in a bidimensional Wigner crystal (WC) structure, as a configuration of minimal free energy. However, because in the WC theory ionic correlations are only considered at the level of a two dimensional electrons liquid at zero temperature, this approach leads to incorrect conclusions. For example, it is predicted that CR decreases by increasing surface charge density (see Fig. 3 in ref. 13) whereas molecular simulations show the opposite. Nevertheless, WC theory has a good agreement with non-zero Monte Carlo simulations of a two-dimensional electron liquid and zero temperature molecular dynamics calculations of a two-dimensional layer of adsorbed ions. The role of entropy in the attraction of like-charged particles has been recognized in the past. Here we will analyze the effect of electrostatic and short range correlations on macroions adsorption at interfaces. A decreasing of the system entropy always produces an increasing of macroions adsorption. Thus, it is concluded that self-assembling at interfaces, CR, CI and like-charged attraction are mainly ruled by entropy.

For the present study we consider a uniformly charged planar surface with $\sigma_0$ charges per unit area contiguous to a macroions solution. In our model, we include the two relevant forces of the system: the long range coulombic interaction and the hard-core interaction forces. Therefore macroions are considered to be charged hard spheres (with charge $Q = Ze$), diameter and number density $\rho$, being $e$ the electronic charge) plus an additional amount ($\rho_c$) of neutralizing counterions (with charge $q = ze$ and radius $r_0 = a_c/2$). The mixture is embedded in a continuous media of dielectric constant $\epsilon$, set equal to that of the charged surface in order to avoid image charges. By the electroneutrality condition $-\sigma_0 = \int_0^\infty \rho_{el}(x) dx$ with $\rho_{el} = \sum_{i=1}^2 \rho_i(x)$, and $\rho_i(x)$ being the local concentration profile of the $i$-th species. Our model is an extension to that considered by Kjellander and Greberg. The WC theory has some similarity with our model. However, whereas we use direct (macroion-macroion, macroion-counterion and macroion-wall) coulombic interactions, in WC screened interactions are used. More importantly, short range correlations and entropy (of fundamental importance for finite temperature calculations) are included in our theory.
Therefore, PB does not describe correctly many of the adsorption phenomena.

In a system at constant volume \( V \), fixed particle number \( N \) and \( T \), its entropy is given by

\[ S = S_{\text{id}} + k \left( \frac{\partial \ln Z}{\partial T} \right)_{N,V}, \]

where \( S_{\text{id}} \) is the ideal gas entropy and the configurational integral \( Z_N = \int \cdots \int \exp \{ -\beta U_N \} \, dx_1, \ldots, dx_N \), being \( U_N \) the potential energy of the \( N \) interacting particles. The exact computation of \( S \) is not an easy task. However, from the expressions for \( S \) and \( Z_N \) it is clear that: (i) the accessible volume decreases as the volume fraction \( (\eta V = \frac{\pi}{6} \sum_i \rho_i a_i^3) \) increases. Thus, the larger \( \eta V \) the lower the entropy. (ii) Electrostatic interactions between like-charged particles also reduce the system number of accessible configurations (hence entropy) by increasing the strength of the coulombic coupling interaction \( \xi = \frac{e^2}{\epsilon a_i} \). Less entropy always implies higher order, which in an inhomogeneous fluid translates in higher adsorption, as we will show. In this picture it is plausible charge reversal by monovalent ions, macromolecular adsorption on uncharged (or like-charged) surfaces, as well as the strong dependence of CR on \( \eta \). These effects can not be explained only with energy arguments.

We will discuss our results in terms of \( g_i(x) \), the local net charge per unit area \( \sigma(x) = \sigma_0 + \int_0^x \rho_\text{el}(y) \, dy \) and the absolute maximum of this function \( (\sigma^* = \max \{ \sigma(x) : x \in [0, \infty) \}) \); with the charge profile given by \( \rho_i(x) \equiv \sum_{m=1}^{2} c_{zm} \rho_m g_m(x) \). The effective electrostatic force on an ion is \( f_i^\text{el}(x) \equiv 2 \pi q_i \sigma(x) \). Therefore, \( \sigma(x) \) not only quantifies charge adsorption but also the wall-particle effective electrical force. We have solved HNC/MSA for several values of \( Z \) and \( \rho \). In all cases the little ions (counterions) are monovalent, i.e., \(|z_c| = 1\). In all our calculations we have used fixed values of \( a = 4 \text{nm}, \sigma_c = 0.4 \text{nm}, T = 298K \) and \( \epsilon = 78.5 \). We present results for macromolecules...
next to positively charged, negatively charged and uncharged surfaces. We study the influence on macroions adsorption of σ₀, Z, η.

In Fig. 1 we show the macroions reduced concentration profile (RCP) for negative macroions (Z = 20, i.e., Q = 20e < 0) next to a positively charged surface (σ₀ = 0.03C/m²) for three different macroions concentrations (η = 0.002, 0.01, 0.05). The macroion RCP shows a very strong adsorption to the wall and a considerable amount of counterions surrounding macroions: In all figures, the counterions RCPs are not plotted for clarity. A second layer of macroions is adsorbed mediated by counterions. In the inset we show the corresponding σ(x) functions: At a distance of one macroion radius a deep minimum is observed, corresponding to a very strong CR. For η = 0.05, the maximum located around x = 3σ₀ shows a CI. In the inset, the maximum located at x = α/2 indicates that small positive ions are adsorbed to the wall. Hence, positive charge is accumulated next to the positively charged surface. We denominate this effect as overcharging. This effect is energetically unfavorable, thus, it must be attributed to the short range correlations since it increases with η. This prediction agrees qualitatively with computer simulation of Tanaka and Grosberg [3]. The effective wall electrical field, which is proportional to σ(x), is positive before the first layer of macroions and then negative, before the second layer. Therefore, the electrical force is first attractive and then repulsive to negative ions. The behavior of the total force on an ion of species i, however, is implicit in the RCP, i.e., a g₁(x) above (below) 1 implies that Fᵢ(x) is attractive (repulsive).

Some of the physics of macroions adsorption is not explicit when considering macroions adsorbed on oppositely charged surfaces. In Fig. 2 we show the macroions RCP for negative macroions (Z = 20) next to a negatively charged surface (σ₀ = −0.03C/m²). Counterions adsorb on the charged surface (not shown) and, for sufficiently high values of ηₕ, a layer of macroions is adsorbed to the wall, after a relatively large void of macroions. Hence a surface CR is induced by little ions (according to the σ(x) functions in the inset) and they, in turn, induce macroions adsorption and the formation of the macroions layer. For sufficiently low values of η = \frac{1}{α}ρ₀a³ there is no macroions adsorption. The qualitative agreement of our Fig. 2 results for η = 0.01, with Monte Carlo data reported in ref. [4], is encouraging. From Figs. 1 and 2 it is seen that higher ηₕ produces higher adsorption. This prediction is in agreement with computer simulations [3, 4, 14, 15].

In Fig. 8 the RCP are shown for negative macroions next to an uncharged surface. For this macroions volume fraction (η = 0.05) we observe colloids adsorption even for low charged colloids [as low as Z = 1 (not shown)]. Since the wall is uncharged, the strong macroions adsorption and wall overcharging is due to the low system entropy, which in this case is due to both: high η and high ξ. Increasing Z increases (ξ), and thus decreases the entropy and increases macroions adsorption and inducing a surface charge. This induced charge is in agreement with the nanoparticles halo reported by Tohver [2], which seems to be a new colloidal stabilization mechanism. Our results show that there is not a minimum surface or macroions charge for the occurrence of CR. Therefore, the assembled nanostructures at interfaces are stabilized by entropy-induced attractive forces, rather than the surface-macroions electrostatic correlations as it is proposed in the the WC theory. These findings are in agreement with experiments on polyelectrolyte adsorption where it is found that CR of a charged substrate “is more a property of the polymer than a property of the surface” [1], and with previous theoretical results, where the importance of particle’s excluded volume (entropy) is recognized as an attractive force mechanism between like charged particles [13]. Please notice that CR in Fig. 2 through Fig. 8 is of the same order of magnitude whether the substrate charge is positive, negative or zero.

In Fig. 4 σ*/σ₀ is plotted as a function of Z for η = 0.002, 0.01, 0.05, for both σ₀ = −0.03C/m² and σ₀ = 0.03C/m² (in the inset). For σ₀ = −0.03C/m², macroions and surface are both negatively charged, and CR is carried out by the small counterions (see discussion of Fig. 2). Nevertheless σ*/σ₀ strongly depends on η, being negligible for low η. For σ₀ < 0, σ*/σ₀ monotonically increases as Z with a positive concavity (\frac{d²σ^*/σ₀}{dZ²} > 0) whereas for σ₀ > 0 \frac{d²σ^*/σ₀}{dZ²} < 0. These results imply that oppositely charged macroions are much more efficiently adsorbed into a charged surface. Our results for oppositely-charged macroions resemble those
shown in Fig. 3 of ref. [13] (WC theory) where \( \frac{\sigma^*}{\sigma_0} \) increases in the same way with \( Z \) and \( \frac{1}{\sigma_0^2} \frac{d^2 \sigma^*}{dz^2} > 0 \). However, the role of entropy is not properly considered in the WC theory [13]: in WC there is a minimum in \( \sigma_0 \) and \( Z \) must be large to have overcharging which is in opposition to computer simulations [14] and our theory. When entropy is considered we observe the following: i) \( \frac{\sigma^*}{\sigma_0} \) depends more strongly on \( \eta \) than on \( Z \) [22]. ii) For a sufficiently high value of \( \eta \) our theory predicts \( \sigma^* > 0 \), even for \( Z = 1 \), independently of the value of \( \sigma_0 \) (even for \( \sigma_0 = 0 \), see Fig. 4). iii) Although not shown explicitly, we found that \( \frac{\sigma^*}{\sigma_0} \) (i.e., CR) increases by increasing \( |\sigma_0| \) (positive or negative, not shown), which is in agreement with recent simulations results [14, 15] and, as we pointed out above, in opposition to the WC theory.

From Figs. 2 to 4 it is clear that macroions adsorption strongly depends on \( \eta \). This effect is far more important for CR than surface or ionic charge. In an experiment of macroion adsorption on a Langmuir film of amphiphilic molecules Rondelez [2] finds that macroions adsorption is increased (hence CR increases) as the lipid layer charge density decreases, by increasing the surface area. This is consistent with our results since an increase of the area per molecule decreases the surface charge density but not the macroions adsorption which is strongly driven by macroions excluded volume. According to this the CR should also increase by increasing the macroions size and/or concentration. In another important experiment Rädler et al. find that the effective charge on DNA-cationic liposome complexes depends on the DNA-to-cationic lipid mixing ratio, i.e., for a certain DNA-to-DNA distance, \( d_{DNA}=d_{iso} \), the complex is neutral. However, if the DNA solution concentration is increased \( d_{DNA} \) becomes lower than \( d_{iso} \), which implies higher DNA adsorption on the membranes, i.e., CR on the membrane. This effect can not be explained by energy arguments, but according to our findings an increase in macroion concentration produces higher adsorption.

In summary, a model for macroions solution next a charged surface has been considered. We found that entropy plays a fundamental role in macroions adsorption phenomena and, in consequence, for assembly of organized nanostructures at interfaces. Some of our predictions seem to be in agreement with previous theoretical studies of polyelectrolyte solutions [15], computer simulations [3, 4, 14] and experimental results [1, 2, 4, 10].

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* Electronic address: fangeles@www.imp.mx
† Electronic address: marcelo@www.imp.mx
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[21] The accessible volume is defined as the free unoccupied volume left by the fluid particles.

[22] While an increment of $\eta$ (say by a given factor) strongly increases $\sigma^*/\sigma_0$, an increment of $Z$ (by the same factor), does not produce a comparable increment.