Free Energy Formalism for Particle Adsorption

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The equilibrium properties of particles adsorption is investigated theoretically. The model relies on a free energy formulation which allows to generalize the Maxwell-Boltzmann description to solutions for which the bulk volume fraction of potentially adsorbed particles is very high. As an application we consider the equilibrium physical adsorption of neutral and charged particles from solution onto two parallel adsorbing surfaces.

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I. INTRODUCTION

The adsorption phenomena, due to the electrochemical interaction between the particles of a system and a surface, is present in many experimental set up, such as the adsorption of a perfect gas on a surface [1] or of charged particles in an electrolyte [2]. In many physical or chemical system, a better understanding of the theoretical equilibrium properties of the adsorbed particles on a surface (see [3] and references therein) would thus be useful to interpret the experiments. Several works have been devoted to this question and various models of particles distribution have been proposed. Among these, many assumed a Maxwell-Boltzman particle distribution (see [3][4] [5]). [3], for instance, study the ionic adsorption on a surface due to some electrochemical forces in order to determine the surface density of adsorbed charges versus the thickness of the sample. This work helps to understand the thickness dependence of the anisotropic part of the anchoring energy experimentaly observed [6] in a nematic liquid cristal [4][7][8].

However, a limit can be made about the Maxwell-Boltzman distribution. Actually, this distribution can only correctly describe the distribution properties in the dilute regime. But even in this regime, the density is usually large at the surface itself, exept when the affinity of the particle for the surface is weak. To overcome the restriction to the first limit, the dilute case, we propose to apply a free energy formalism to the study of the equilibrium properties of neutral and charged particles adsorption onto two parallel adsorbing surfaces. Another advantage of the free energy formalism lays in the fact that it leads to the generalized Poisson-Boltzmann equation introduced in [10] which takes into account the finite size of the ions. In that paper the behavior of electrolytes solutions closed to a charged surface was studied. In our work, the surface is rather charged by the adsorption of one of the two charges present in the system. Within our framework we obtain the electric potential distribution from the generalized Poisson-Boltzmann equation, the correct equations for the bulk particle distribution and the density of the particles on the surface with respect to the thickness d of the sample. For small thickness, the d dependence of the electric potential and of the chemical potential are determined and it is found that the surface density is proportional to thickness. Whereas in the limit of large d the electric potential and the surface density are independent of the thickness. It is nevertheless clear that results obtained with the phenomenological, coarse-grained free energy formalism to systems approaching molecular dimension can only be trusted as far as general trends are concerned.

It is important to note that in the context when several kind of particles are present in the system, as it would be in an electrolyte, we find a particle distribution different from the Fermi-Dirac like distribution introduced in [9]. Actually, the Fermi-Dirac distribution takes naturally into account the occupation of the adsorption sites. Yet it misses the mixing entropy contribution which is present in our formalism. As a consequence, we show that in the limiting case of a weak electrolyte, the results of the Poisson-Boltzmann approach are recovered by our formalism but not by the Fermi-Dirac distribution.

The paper is organized as follows. In section 2 we introduce the mean field free energy formalism for neutral particle in a isotropic fluid limited by two adsorbing surfaces. In the same section the case of the adsorption competition between two neutral particles is studied. In section 3 we generalize the free energy formalism to the study of the ionic adsorption in a isotropic fluid limited by two adsorbing surfaces, already studied by means of the Fermi-Dirac distribution in [3] and [9].

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II. NEUTRAL PARTICLE ADSORPTION

A. Theory on a lattice

Consider N neutral particles in a slab of thickness d delimited by two surfaces of area S. We divide the slab into discrete cells of size a^3 (the size of the particle) and each cell is limited to a single particle occupation. We call N_b the number of sites in the bulk and N_s the number of surface adsorption sites. In thermodynamic equilibrium, n_b and n_s are the number of particles in the bulk and at the surface respectively. The volume fraction is then $\phi = n_b/N_b$ and the surface density $\phi_s = n_s/N_b$. The conservation of the total number of particle $N = n_s + n_b$ is also written:

$$\Phi = 2\phi_s \frac{a}{d} + \phi(1 - \frac{2a}{d}) \tag{1}$$

which is valid if the bulk volume fraction is uniform. If this fraction is not uniform (see section 3), relation (1) becomes:

$$\Phi = 2\phi_s \frac{a}{d} + \frac{1}{d} \int_{-(d-2a)/2}^{(d-2a)/2} \phi(x) dx \tag{2}$$

where Φ is the total volume fraction.

B. Free energy formalism

We will use the free energy formalism for the particles adsorption. It has been first introduced by D. Andelman et al. (for a review see [11]) to describe the kinetic adsorption of surfactant. This theoretical approach was successfully applied to the kinetic of non-ionic and ionic surfactant adsorption as well as to the kinetic of surfactant mixture adsorption. In this formalism, the two equations describing both the diffusive transport of surfactant molecules from the bulk solution to the interface and the kinetic of adsorption at the interface itself are derived from a single functional. The scope of the present paper is to apply the free energy formalism to the study of the equilibrium properties of particles adsorption.

Following [11] we write the total free energy as a functional of the volume fraction in the bulk $\phi(x)$ and the density at the interface ϕ_s

$$\frac{F(\phi)}{S} = 2f_s(\phi_s) + \int_{-(d-2a)/2}^{(d-2a)/2} f\left[\phi\left(x\right)\right] dx \tag{3}$$

where the bulk free energy density is written:

$$f(\phi) = \frac{1}{a^3} \left\{ kT\left[(\phi \ln \phi + (1-\phi)\ln(1-\phi)\right] - \frac{\widetilde{\beta}}{2}\phi^2 - \widetilde{\mu}\phi \right\} \tag{4}$$

and the surface free energy density is equal to :

$$f_s\left(\phi_s\right) = \frac{1}{a^2} \left\{ kT\left[\phi_s \ln \phi_s + (1-\phi_s)\ln(1-\phi_s)\right] - \widetilde{\alpha}\phi_s - \frac{\widetilde{\beta}}{2}\phi_s^2 - \widetilde{\mu}\phi_s \right\} \tag{5}$$

The parameters $\widetilde{\alpha}$ accounts for the energetic preference of the particle to absorb on the surface. $\widetilde{\beta}$ is the lateral interaction between two adjacent charges. Note that the main difference with the free energy introduced in [11] in the context of surfactant adsorption lies in the presence of the exact entropic term in (4) rather than on an approximate term. Actually, below as well as above the critical micellar concentration, the free chain surfactant solution is always dilute, so that a good approximation for the entropic term is $S = \phi \ln \phi - \phi$. Another difference is due the effect on the finite volume: in (4) and (5) $\widetilde{\mu}$ is the chemical potential at equilibrium. Its value is not imposed by an external reservoir but is determined by the conservation equation (1). In the infinite volume case considered in [11], the chemical potential is imposed by an external reservoir localized at infinity. This last condition imposes the equilibrium bulk volume fraction.

The variation of F with respect to $\phi(x)$,that is

$$\frac{\delta F}{\delta \phi\left(x\right)}=0 \tag{6}$$

yields the bulk equilibrium volume fraction

$$\phi\left(x\right)=\phi=\frac{1}{1+e^{-\mu-\beta\phi}} \tag{7}$$

in which we introduce the dimensional quantities $\beta=\widetilde{\beta}/kT$ and $\mu=\widetilde{\mu}/kT$. At the surface the condition

$$\frac{\delta F}{\delta \phi_s}=0 \tag{8}$$

yields the equilibrium adsorption isotherm

$$\phi_s=\frac{1}{1+e^{-\mu-\alpha+\beta\phi_s}} \tag{9}$$

with $\alpha=\widetilde{\alpha}/kT$.

Considering the case $\beta=0$, we find the Fermi-Dirac distribution that can also be written

$$\phi_s=\frac{\phi}{\phi+\left(1-\phi\right)e^{-\alpha}} \tag{10}$$

For $\beta=0$, the number of particles conservation (1) allows to compute analytically the chemical potential :

$$e^{-\mu}=-a+\sqrt{a^2+b} \tag{11}$$

where

$$a=\frac{\left[\Phi-\left(1-2a/d\right)\right]+\left(\Phi-2a/d\right)e^{\alpha}}{2\Phi} \tag{12}$$

$$b=\frac{\left(1-\Phi\right)}{\Phi}e^{\alpha} \tag{13}$$

Note that for $d=2a$ we can check that $e^{-\mu}=e^{\alpha}\left(1-\Phi\right)/\Phi$ which leads to the expected result $\phi_s=\Phi$, since all particles are localized on the surfaces.

1. Case $\Phi >> 2a/d$

The condition

$$1>\Phi>>2a/d \tag{14}$$

yields for the chemical potential

$$e^{-\mu}=\frac{\left(1-\Phi\right)}{\Phi} \tag{15}$$

and a bulk volume fraction of :

$$\phi=\Phi. \tag{16}$$

Condition (14) implies a negligible variation of the equilibrium volume fraction after the adsorption process. At the surfaces,

$$\phi_s=\frac{\Phi}{\Phi+\left(1-\Phi\right)e^{-\alpha}} \tag{17}$$

is independent of the size d. Even if the surface density of particles is large, the sample is large enough to ensure that the bulk volume fraction does not change. This result can also be obtained from the particle number conservation equation (1) $\Phi=2\phi_s\frac{a}{d}+\phi(1-\frac{2a}{d})$ which in the limit $d\rightarrow\infty$ gives $\phi=\Phi$.

2. Case $\Phi << 2a/d$

This condition corresponds to a dilute regime $\Phi << 1$, where $\phi << 1$ so that $\mu \approx \ln \phi$. The surface coverage can then be written

$$\phi_s = \frac{\phi}{\phi + e^{-\alpha+\beta\phi_s}} \tag{18}$$

or from the particle number conservation

$$\phi_s = \frac{d\Phi - 2a\phi_s}{d\Phi - 2a\phi_s + (d-2a)\, e^{-(\alpha+\beta\phi_s)/T}} \tag{19}$$

The dilute regime for $\beta = 0$ is of some interest. For a dilute solution the chemical potential (11) is approximatively

$$e^{-\mu} \approx \frac{1 + 2a/d(e^{\alpha} - 1)}{\Phi} \tag{20}$$

leading to :

$$\phi \approx \frac{\Phi}{1 + 2a/d\,(e^{\alpha} - 1)} \tag{21}$$

and, at the surface

$$\phi_s \approx \frac{\Phi}{2a/d + e^{-\alpha}\,(1 - 2a/d)} \tag{22}$$

Note that this relation can also be obtained from equation (19).

If $d << 2ae^{\alpha}$, ϕ is negligible and (22) becomes

$$\phi_s \approx \Phi \frac{d}{2a} \tag{23}$$

that is the surface coverage increases linearly with the size of the sample. Note that in paper [9] the same expression was written

$$\phi_s \simeq \frac{N}{2N_s} d \tag{24}$$

where N is bulk density of particles in the absence of adsorption and N_s is the surface density of sites. With the identifications $\Phi = Na^3$ and $N_s = 1/a^2$ the two expressions (23)and (24) coincide. But, as the authors of [9] did not introduce a lattice, expression (24) leads to the unphysical result $\phi_s \to 0$ in the limit $d \to 0$, since the correct limit $d \to 2a$ is hidden. Note that this problem will be even more apparent in the case of the ionic adsorption.

In the opposite limit $d >> 2ae^{\alpha}$ from (21) we deduce for the volume fraction in the bulk

$$\phi \approx \frac{\Phi}{1 - 2a/d} \approx \Phi \tag{25}$$

which imposes : $\phi_s \frac{2a}{d} << \Phi$. Actually, from (22) we see

$$\phi_s \approx \frac{\Phi}{e^{-\alpha}} \tag{26}$$

from which we deduce

$$\phi_s \frac{2a}{d} << \Phi \tag{27}$$

In this case the sample is large enough so that the volume fraction can be considered as constant even when the surface density is large. The system is then equivalent to an infinite system coupled to an external reservoir, this last one keeping the volume fraction constant. We see a crossover between a regime where the surface coverage increases linearly and another regime in which the surface coverage is independent of thickness.

C. Equilibrium distribution of two kinds of neutral particles

In this section, we consider an infinite system composed of two neutral species which can both adsorb on a flat surface.

We generalize the free energy formulation designed in the preceding section by writing the bulk contribution of the density free energy in kT units

$$f(\phi_A,\phi_B) = \frac{kT}{a^3}\{\phi_A\ln\phi_A+\phi_B\ln\phi_B+(1-\phi_A-\phi_B)\ln(1-\phi_A-\phi_B) \tag{28}$$

$$-\frac{\beta_A}{2}\phi_A^2-\frac{\beta_B}{2}\phi_B^2-\varepsilon\phi_A\phi_B-\mu_A\phi_A-\mu_B\phi_B\Big\} \tag{29}$$

where ε is an interaction between the two species. At the surface, we have :

$$f_s(\phi_{s,A},\phi_{s,B}) = \frac{kT}{a^3}\{\phi_{s,A}\ln\phi_{s,A}+\phi_{s,B}\ln\phi_{s,B}+(1-\phi_{s,A}-\phi_{s,B})\ln(1- \tag{30}$$

$$\phi_{s,A}-\phi_{s,B})-\alpha_A\phi_{s,A}-\alpha_B\phi_{s,B}-\frac{\beta_A}{2}\phi_{s,A}^2-\frac{\beta_B}{2}\phi_{s,B}^2 \tag{31}$$

$$-\varepsilon\phi_{s,A}\phi_{s,B}-\mu_A\phi_{s,A}-\mu_B\phi_{s,B}\} \tag{32}$$

Note the presence of the mixing entropic term $(1-\phi_A-\phi_B)\ln(1-\phi_A-\phi_B)$ in these two expressions. This terms is very important since it avoids that two particles of different kind sit at the same place in the lattice. Its absence would lead to the FD distribution.

Minimizing the free energy, we obtain in the bulk:

$$\phi_A = \frac{1-\phi_B}{1+e^{-(\mu_A+\beta_A\phi_A+\varepsilon\phi_B)}} \tag{33}$$

and

$$\phi_B = \frac{1-\phi_A}{1+e^{-(\mu_B+\beta_B\phi_B+\varepsilon\phi_A)}} \tag{34}$$

whereas at the surface we have:

$$\phi_{s,A} = \frac{1-\phi_{s,B}}{1+e^{-(\mu_A+\alpha_A+\beta_A\phi_{s,A}+\varepsilon\phi_{s,B})}} \tag{35}$$

and

$$\phi_{s,B} = \frac{1-\phi_{s,A}}{1+e^{-(\mu_B+\alpha_B+\beta_B\phi_{s,B}+\varepsilon\phi_{s,A})}} \tag{36}$$

We thus see that the distributions of the two species are not independent of each other, due to the mixing entropy.

Suppose now that $\alpha_A >> \alpha_B$. We find

$$\phi_{s,B} \approx \frac{e^{\mu_B+\alpha_B}}{e^{\mu_A+\alpha_A}} << 1 \tag{37}$$

and

$$\phi_{s,A} = \frac{1}{1+e^{-\mu_A-\alpha_A}} \tag{38}$$

showing that only one specie adsorbs, the other staying in the bulk. One can check that $\phi_{s,A}+\phi_{s,B}$ is always smaller than one.

Now, let us compare our result with the Fermi-Dirac distribution. In such a context, the distribution for the two species are:

$$\phi_{A,B} = \frac{1}{1+e^{-\mu_{A,B}}} \tag{39}$$

for the bulk and

$$\phi_{s,A,B} = \frac{1}{1+e^{-\mu_{A,B}-\alpha_{A,B}}} \tag{40}$$

for the surface. The two distributions are now completely independent. In particular for the $\alpha_A >> \alpha_B$ the sum $\phi_{s,A}+\phi_{s,B}$ is not guarantee to be smaller than 1. This example shows the importance of taking the mixing entropy into account when more than one specie are present.

III. IONIC ADSORPTION

The power of the free energy formalism can also be applied to the ion distribution in an isotropic fluid limited by two adsorbing surfaces. As explained in [3] and [9], this system has already been considered by several authors. Actually, the ionic adsorption has been invoked to explain the thickness dependence of the anisotropic part of the anchoring energy of the interface between a substrate and a nematic liquid crystal.

Consider a slab of thickness d with two identical adsorbing flat surfaces that adsorb only positive ions. Obviously the liquid is globally neutral. However, due to the selective ionic adsorption there is a distribution of charges yielding a non uniform electric potential $V(x)$ across the sample. Since the surfaces are identical i.e. the affinity of the positive ions for the surfaces are identical, the potential is symmetric $V(x) = V(-x)$ and $E = -dV/dx$ is vanishing at the middle of the sample.

The total free energy for a symmetric electrolyte in the mean field approximation has already been introduced in [10] in the context of the adsorption of large ions from a solution of infinite size to a charged surface. In our case it is rather the adsorption phenomena which charges the surfaces. Within the mean-field approximation, the total free energy in the bulk $f = u - Ts$ can be written in terms of the local electrostatic potential in kT unit $\psi(x) = eV(x)/kT$ and the ions volume fraction $\phi^{\pm}(x)$. The electrostatic energy contribution is

$$u = \frac{kT}{a^3}\int dx \left[-L_B^2 \left|\frac{\partial \psi}{\partial x}\right|^2 + \phi^+\psi - \phi^-\psi - \mu_+\phi^+ - \mu_-\phi^- \right] \tag{41}$$

where ε is the dielectric constant of the solution, $\mu_{\pm}$ are the equilibrium chemical potential of the two ions and $L_B = \sqrt{\frac{\varepsilon kTa^3}{2e^2}}$ is the intrinsic length of the problem. Note that we use the same system of unit as [9] which is different from the one of [10] where $L_B = \sqrt{\frac{\varepsilon kTa^3}{8\pi e^2}}$. The first term in the left hand side of (41) is the self energy of the electric field, the next two terms are the electrostatic energy of the ions. For the sake of simplicity we do not introduce additional steric interaction. The entropic contribution is

$$Ts = -\frac{kT}{a^3}\int dx \left[\phi_+ \ln\phi_+ + \phi_- \ln\phi_- + (1-\phi_+-\phi_-)\ln(1-\phi_+-\phi_-)\right] \tag{42}$$

The first two terms represent the tanslational entropy of the ions and the last term the entropy of mixing i.e. the entropy of the solvant molecules.

At the interface itself, the total free energy is obtained by adding an electrostatic contribution $\phi_s^+\psi_s$ to equation (5)

$$\begin{aligned} f_s\left(\phi_s^+, \psi_s\right) &= \frac{kT}{a^2}\left\{\left[\phi_s^+ \ln\phi_s^+ + \left(1-\phi_s^+\right)\ln\left(1-\phi_s^+\right)\right] - \alpha\phi_s^+ + \phi_s^+\psi_s \right. \\ &\quad \left. -\mu^+\phi_s^+\right\} \end{aligned} \tag{43}$$

The total free energy of the system is then:

$$\frac{F(\phi^{\pm})}{S} = 2f_s(\phi_s^+, \psi_s) + \int_{-(d-2a)/2}^{(d-2a)/2} f\left[\phi^{\pm}(x), \psi(x)\right] dx \tag{44}$$

The ions number conservation imposes the equality between the two chemical potentials $\mu_+ = \mu_- = \mu$. The variation of the bulk free energy with respect to $\phi^{\pm}$ yields the volume fraction of the ions in the bulk:

$$\phi^+ = \frac{e^{-\psi+\mu}}{h(\psi,\mu)} \tag{45}$$

and

$$\phi^- = \frac{e^{\psi+\mu}}{h(\psi,\mu)} \tag{46}$$

where

$$h(\psi,\mu) = 1 + 2e^{\mu}\cosh\psi \tag{47}$$

Note that the distribution in the bulk is very different from the FD distribution which reads

$$\phi^{\pm}_{FD} = \frac{1}{1+e^{-\mu\pm\psi}} \tag{48}$$

The variation of the bulk free energy with respect to ψ yields the modified Poisson Boltzman equation introduced in [10] :

$$\nabla^2\psi = \frac{e^{\mu}}{L_B^2}\frac{\sinh\psi}{h(\psi,\mu)} \tag{49}$$

This equation is similar to the expression given in [9]. The difference lies in the formula for $h(\psi,\mu)$ which is in [9] : $h(\psi,\mu) = 1 + 2e^{\mu}\cosh\psi + e^{-2\mu}$.

The variation of the total free energy with respect to $\psi\,(x = d/2) \equiv \psi_s$ yields the requirement of the overall charge neutrality:

$$\left.\frac{\partial\psi}{\partial x}\right|_{x=d/2} = \frac{-1}{L_s}\phi_s \tag{50}$$

where $L_s = a^2\varepsilon kT/e^2$ is a caracteristic length of the surface introduced in [9]. Minimizing the surface free energy ϕ_s yields

$$\phi_s = \frac{1}{1+e^{\psi-\alpha-\mu}} \tag{51}$$

which is a Fermi-Dirac distribution.

Note that a FD distribution is obtained for ϕ^- when the electrostatic potential is very high $\psi >> 1$ since in this case:

$$\phi^- \to \frac{1}{1+e^{-\psi-\mu}} \tag{52}$$

whereas

$$\phi^+ \to e^{-2\psi}\phi^- \neq \frac{1}{1+e^{\psi-\mu}} \tag{53}$$

It is instructive to analyze the behaviour of the system for semi infinite and very thin sample and then to compare the prediction of our model to the results obtained with the FD distribution.

A. Infinite volume limite

In the infinite volume limit $d \to \infty$, we have :

$$e^{\mu} = \frac{\phi_0}{2(1-\phi_0)} \tag{54}$$

whereas

$$e^{\mu}_{FD} = \frac{\phi_0}{2-\phi_0} \tag{55}$$

due to the lack of the mixing entropy. The generalized PB equation can be solved numerically to find the electric field and the ions distributions across the sample. This has been done in [10] where interesting curves can be found.

It is only in the dilute case that the two chemical potential coincide and are equal to the Boltzman one :

$$e^{\mu}_{\text{Boltzman}} = \frac{\phi_0}{2} \tag{56}$$

In this case, we obtain the surface potential

$$\psi_s = \frac{2\alpha}{3} + \frac{2}{3}\ln\left(\frac{L_B}{L_s}\sqrt{\frac{\phi_0}{2}}\right) \tag{57}$$

and the surface coverage :

$$\phi_s = \frac{1}{1 + e^{\alpha/3}\left(\frac{L_B}{L_s}\frac{2}{\phi_0}\right)^{2/3}} \tag{58}$$

in agreement with [9].

1. Small volume limit

In the finite volume case we have two conservation laws

$$\Phi = \frac{2a}{d}\phi_s + \frac{1}{d}\int_{-(d-2a)/2}^{(d-2a)/2} \frac{e^{\mu-\psi}}{1+2e^{\mu}ch(\psi)} \tag{59}$$

$$\Phi = \frac{1}{d}\int_{-(d-2a)/2}^{(d-2a)/2} \frac{e^{\mu+\psi}}{1+2e^{\mu}ch(\psi)} \tag{60}$$

Let us consider the small volume limit $d \to 3a$. Physically, we cannot consider a smaller bound since the negative charges are not adsorbed In particular, it is not possible to take the limit $d \to 0$.

The relation (60) becomes (assuming $e^{\psi_0} \gg 1$, which will be justified later):

$$\Phi \approx \frac{d-2a}{d}\frac{e^{\mu+\psi_0}}{1+e^{\mu+\psi_0}} \tag{61}$$

which leads to :

$$e^{\mu} = \frac{\Phi}{1-\frac{2a}{d}-\Phi}e^{-\psi_0} \tag{62}$$

Considering the approximation :

$$\psi_s \approx \psi_0 - \frac{a}{L_s}\phi_s \tag{63}$$

and the fact that $\frac{a}{L_s}$ is very small, we can assume that :

$$\psi_s \approx \psi_0 \tag{64}$$

in (51), so that :

$$\phi_s \approx \frac{\Phi}{\Phi + \left(1-\frac{2a}{d}-\Phi\right)e^{-\alpha+2\psi_0}}. \tag{65}$$

Plugging this result in (59) and using the fact that $e^{\alpha} \gg 1$ yields the electric potential :

$$e^{\psi_0} \approx e^{\alpha/2}\sqrt{\frac{\frac{2a}{d}-\Phi}{1-\frac{2a}{d}-\Phi}} \tag{66}$$

confirming our assumption $e^{\psi_0} \gg 1$.

For the chemical potential we readily obtain:

$$e^{\mu} \approx \frac{\Phi}{1-\frac{2a}{d}-\Phi}\sqrt{\frac{1-\frac{2a}{d}-\Phi}{\frac{2a}{d}-\Phi}}e^{-\alpha/2}. \tag{67}$$

and for the surface coverage we find :

$$\phi_s \approx \frac{d\Phi}{2a}. \tag{68}$$

These results are very different from the one obtained by Barbero et al. with the Fermi Dirac distribution which are :

$$e^{\psi_0} \sim \frac{e^{\alpha/2}}{d} \tag{69}$$

$$e^{\mu} \sim \sqrt{\Phi} \tag{70}$$

These two last relations do not lead to the result obtained with the Maxwell-Boltzman distribution used in the dilute regime. In other words, the Fermi- Dirac distribution in the limit of a small concentration does not lead to the correct Maxwell- Boltzman result.

On the contratry, our equations (66) and (67), for $\Phi \ll 1$, yields :

$$e^{\psi_0} \approx e^{\alpha/2}\sqrt{\frac{2a}{d-2a}} \tag{71}$$

and

$$e^{\mu} \approx \sqrt{\frac{d^2}{2a\,(d-2a)}}\Phi e^{-\alpha/2} \tag{72}$$

that are the results obtained with a Maxwell-Boltzmann distribution.

An estimation of the parameter was given in [9] for a typical nematic liquid crystal ($\epsilon \approx 6$ for an organic liquid) limited by two glasses. The adsorption energy was evaluated $\alpha \approx 6$ and for a typical molecule of radius $R \approx 40$A one has $L_B \approx 30$A. The surface density was found to be d dependent for thickness smaller than 300 A.

IV. CONCLUSION

In this paper, we have proposed a free energy formalism to describe the phenomenon of surface adsorption of neutral and charged particles as well. This free energy formalism has led to the equilibrium particles distribution for the case of physical adsorption of neutral and charged particles from solution onto two parallel adsorbing surfaces. In particular, we have found the correct equations for the electric potential and the equilibrium charge distribution with respect to the thickness of the electrolyte sample in case of high bulk concentration and we recover the results obtained with the Maxwell-Boltzmann distribution in the limit of small concentration.

We are aware that our model relies on some strong assumptions, in particular the adsorbed particles are confined to a monomolecular layer whereas multilayer adsorption is frequently observed. Moreover, we have assumed that the surface is homogenous which is obviously not the case in general.

Nevertheless,one of the advantages of the free energy formalism is that it relies on a minimization principle, avoiding in this way the introduction of ad-hoc distributions, and allowing straightforwardly the description of multi particles adsorption. Moreover it can be extended to take into account the particles interactions in the bulk and at the surface itself, that are usually not considered. This generalization needs further investigation.

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