

The Interaction between a Charged Wall and Its Counterions: A Condensation Theory

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We use the theory of counterion condensation to calculate the potential of mean force between a charged planar wall and an oppositely charged ion of unsigned valence Z . We find two solutions to this problem, an outer potential when the Z -ion is relatively far from the wall and an inner one when it is relatively close. There is a discontinuous upward jump from one to the other branch, as the Z -ion approaches the wall. The jump must occur at the wall itself, and we attribute it to interaction with the condensed layer of counterions which resides on the wall. At an infinitesimal distance from the wall, the Z -ion encounters a repulsive force resisting penetration of the condensed layer. Then, when the Z -ion penetrates the condensed layer, Z univalent counterions are released from the condensed layer into the bulk solution, maintaining the effective charge on the wall at an invariant critical value. We discuss the possible connections of the theory with published data from molecular dynamics simulations on lipid bilayers.

I. Introduction

Nanotechnological applications,¹ interesting observations at the glass–water interface,^{2,3} as well as investigations into the structure and function of cellular phospholipid bilayers⁴ provide motivation for attempts at accurate descriptions of the ionic environment of charged surfaces with globally planar geometry. As reviewed several years ago by Berkowitz et al.,⁵ molecular dynamics simulations have emerged as a major tool in studying the interactions of the phospholipid polar headgroups with water and ions on a detailed molecular level, stimulating attempts to bring the classical theory of charged planar surfaces^{6,7} to a more realistic level.^{8–10} In previous papers, we have generalized the counterion condensation theory of locally rodlike polyelectrolyte chains^{11,12} to include planar and spherical surfaces.^{13,14} We continue this project here and try as well to make some connections with recent molecular dynamics simulations of lipid bilayers.

The analysis of counterion condensation theory concludes that counterions are distributed around sufficiently highly charged macroions in two spatially distinct populations. An inner population is condensed on the macroion. An outer distribution is more diffuse, forming a Debye–Hückel-like ionic cloud. This description, strongly supported by experimental data on polyelectrolytes¹⁵ and direct visual evidence from simulations of DNA,^{16,17} appears to be accurate as well for large spherical particles.¹⁸ The condensed layer of counterions emerges when the bare charge density of the macroion exceeds a critical value, and it maintains the effective charge density—the net charge after condensation—at the critical value. Applied electric fields sense the effective charge,^{18,19} an indication that the condensed counterions are intimately involved with the microscopically solvated, mesoporous structure of the macroion surface.

Data on the effective DNA charge from single-molecule force measurements¹⁹ would have been difficult to interpret had they not been in agreement with the predictions of counterion condensation theory. It is not so much that the measured value

of the effective charge agrees with prediction as that this value is otherwise quite unreasonably observed to be independent of ionic strength over a remarkably wide range. For DNA, the theory in fact predicts a constant value up to about 1 M salt,^{11,12} as found.¹⁹

Invariance in the face of large variations of ionic strength is a feature, however, only of two-dimensional geometries (rodlike macroions). For rodlike polymers, as well as for flexible ones (since Debye-length segments of flexible polymers are more or less rodlike), theory predicts counterion condensation as a consequence of successful competition between the unfavorable $-\ln C$ energy of ionic dissociation from the oppositely charged rod and the favorable $-\ln C$ entropy of counterion dissociation into the spacious bulk. It was a surprise, then, when a related argument went through for spheres (the same favorable dissociation entropy but a noncompetitive association energy) and for planes (the same entropy but a dominating energy).^{13,14} In both cases, for nonvanishing counterion concentrations, we found supercritical bare surface charge densities on which counterions condensed to yield fractional, but ionic-strength-dependent, effective charges. Only in the limit of zero ionic strength do spheres condense none of their counterions (the critical bare charge density becomes infinite like $-\ln C$) and planes condense all of theirs (the critical charge density tending to zero like $-\sqrt{C \ln C}$), regardless of how high the bare charge density (spheres) or how low (planes).¹³

In this paper, we continue to explore these alternate geometries. As mentioned, we have found the existence of an ionic-strength-dependent critical bare charge density on a planar wall.¹³ For bare charge densities higher than critical, counterions condense on the wall until the effective charge equals the critical charge. In the limit of zero ionic strength, the critical charge density, and hence the effective charge, is zero; the wall has condensed all of its counterions. For low but nonzero ionic strengths, the effective charge is a nonvanishing fraction of the bare charge, so that the two kinds of counterions, condensed and uncondensed, are manifest. Here, we calculate the potential of mean force for a counterion as a function of its distance from the wall. We find two branches of the potential, corresponding

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to the two counterion populations. The transition from one branch to the other as a counterion approaches the wall is singular and must occur at the wall itself.

II. The Equilibrium Condition and Its Two Solutions

We begin by recording from linearized electrostatics the bare Debye–Hückel potential of mean force between a charged point ion with unsigned valence Z and an oppositely charged impenetrable wall. It is instructive to consider the planar wall as a limiting case of a large impenetrable sphere. Let the radius of the sphere be a , and suppose that it bears a uniform surface charge $\pm Ne$, where e is the elementary charge. The distance from the Z -ion to the center of the sphere is r , and the distance x between the point Z -ion and the nearest point on the spherical surface is $x = r - a$. The expression for the dimensionless Debye–Hückel potential of mean force (in units of $k_B T$, the product of Boltzmann constant and Kelvin temperature) is⁶

$$-ZNl_B \frac{e^{-\kappa x}}{(1 + \kappa a)(a + x)} \quad (1)$$

where $l_B = e^2/4\pi D\epsilon_0 k_B T$ is the Bjerrum length (ϵ_0 is the permittivity of free space, and D is the dielectric constant). The Debye screening length is $1/\kappa$, where $\kappa^2 = 4\pi l_B \sum_i (N_i/V) z_i^2$; the sum runs over small ion species in solution of volume V , N_i is the number of ions of species i , and z_i is their unsigned valence. If the ions originate from a single dissociating salt of concentration $C = N_s/V$, where N_s is the number of formal electroneutral salt “molecules” in solution, then the expression for κ^2 reduces to $4\pi l_B C(v_1 + v_2)z_1 z_2$, where v_i is the number of ions of species i in the chemical formula for the bi-ionic salt. Thus, the Debye screening length κ^{-1} is inversely proportional to \sqrt{C} .

We obtain the potential for the wall by allowing the sphere radius a to become infinite, which means $\kappa a \gg 1$, and $x/a \rightarrow 0$, for fixed separation x between the Z -ion and the surface. Moreover, we will always use σ to represent the number density of elementary charges on the surface of the wall (as distinct from charge density), so that N can be replaced by $4\pi a^2 \sigma$, resulting in the cancellation of a from the expression for the Debye–Hückel potential $w(x)$ per unit charge on the wall

$$w(x) = -\frac{4\pi l_B \sigma Z}{\kappa} e^{-\kappa x} \quad (2)$$

(For a charged plane bathed on both sides by solvent and small ions, and permeable to them, the corresponding potential is decreased by a factor of 2 from the ion–wall potential, as follows from an application of Gauss’s flux theorem.)

The calculation of the nonlinear counterion condensation potential analyzes the electrostatic free energy G (made dimensionless by use of $k_B T$ units) into three components, the self-interaction of the charge on the wall, the work required to transfer counterions from bulk to the condensed layer, and the interaction between the wall and the Z -ion, $G = G_{\text{self}} + G_{\text{transfer}} + G_{\text{ion-wall}}$

$$G_{\text{self}} = 2\pi N(1 - z\theta)^2 \frac{l_B \sigma}{\kappa} \quad (3)$$

$$G_{\text{transfer}} = N\theta \ln \frac{\theta}{\gamma \nu C Q} \quad (4)$$

$$G_{\text{ion-wall}} = (1 - z\theta)Nw(x) \quad (5)$$

In these expressions, the factor $1 - z\theta$ accounts for reduction of the bare charge on the wall by counterion condensation, where θ is the number of counterions condensed per bare charge on

the wall and z is the unsigned valence of the counterions. It appears squared in G_{self} but only linearly in $G_{\text{ion-wall}}$, since it is the bare Z -ion that interacts with the wall. In G_{transfer} , C is the added salt concentration (defined in the first paragraph of this section and elaborated there in its relation to the Debye screening length), which we take in excess over the counterions deriving from the wall charges. The solution contains only a single salt, one of the constituents of which is the same species as the counterions from the wall. There are ν such counterions in the chemical formula for the salt, so that $\gamma \nu C$ is the activity of counterions in the solution bulk, where γ is an activity coefficient (the factor $\gamma \nu$ cancels from our final result). The quantity Q is the internal partition function of the condensed counterion layer, assumed independent of θ . This latter assumption means that we neglect short-range interactions among the condensed counterions, such as finite-size effects. The long-range electrostatic effects of the condensed layer are subsumed in G_{self} and $G_{\text{ion-wall}}$.

The condition determining the equilibrium value of the number of condensed counterions is $\partial G/\partial \theta = 0$, which we write out

$$4\pi z(l_B \sigma/\kappa)(1 - z\theta) + \ln Q - \ln(\theta/\gamma \nu) - 1 + zw(x) = -\ln C \quad (6)$$

The physical origin of the $-\ln C$ term on the right-hand side is the entropy of dissociation of counterions from the wall into the bulk solution. We note that it diverges to plus infinity if $C \rightarrow 0$, implying a dominant tendency for complete dissociation unless the entropy is fully counteracted by some other effect that favors counterion association with the wall. That is, the counterion condensation fraction θ must vanish along with C unless a “binding energy” is present and becomes negatively infinite as $C \rightarrow 0$ in such manner as to compensate for the infinite dissociation entropy.

Let us look at each term on the left-hand side, starting with the third one involving $-\ln \theta$. A conventional mass-action analysis would require the fractional number of condensed counterions θ to approach zero in proportion to C , and indeed, this requirement does cancel the $-\ln C$ entropy divergence. However, we then find that both the proportionality constant and the partition function Q are indeterminate. We must look elsewhere for a complete solution.

We will assume that the internal partition function Q of the condensed layer is regular (to be justified *a posteriori*), so the second term on the left side does not diverge. The term $zw(x)$ is a binding energy, but it does not diverge. The justification of this statement requires inspection of eq 2. The ratio σ/N equals the inverse of the area of the wall. The wall is infinite in extent, so each dimension of it must be much larger than the screening length $1/\kappa$. The ratio $(\sigma/N)\kappa^{-1}$ that appears in the expression for $w(x)$ in eq 2 is therefore much less than κ , which itself vanishes like \sqrt{C} in the limit $C \rightarrow 0$.

We are left looking closely at the first term on the left-hand side of the equilibrium condition. It is also a “binding energy”, since it originates from the self-electrostatic free energy of the wall, which is decreased by counterion condensation. Suppose that the surface density σ of unit charges on the wall is continuously adjusted upward as C tends to zero in such a way as to compensate the increasing dissociation entropy. In fact, this maneuver provides two solutions to our problem, as we will show.

We search for an “outer” solution and an “inner” solution. The physical characteristic of the outer solution is that the Z -ion is sufficiently far from the wall as not to influence the number

of counterions condensed on the wall. The inner solution pertains to closer distances at which the presence of the Z-ion does change the number of condensed counterions.

To get the outer solution, we rewrite the equilibrium condition,

$$4\pi z(l_B\sigma/\kappa)(1 - z\theta) = -\ln C - \ln Q + \ln(\theta/\gamma\nu) + 1 - zw(x) \quad (7)$$

This equation is exactly the same as eq 6 but with nondivergent terms shifted from the left- to the right-hand side of the equation. As $C \rightarrow 0$, we continuously adjust the surface density σ such that the left-hand side of eq 7 diverges like $-\ln C$

$$4\pi z(l_B\sigma/\kappa)(1 - z\theta) = -2 \ln \kappa/\ell \quad (8)$$

Here, ℓ is a constant length small enough that κ/ℓ is a small quantity but otherwise arbitrarily chosen. In a previous paper, we used the Bjerrum length l_B for this purpose, but $-\ln \kappa/\ell$ is asymptotically equal to $-\ln \kappa l_B$ as $C \rightarrow 0$ for any constant value of ℓ . This equation may be solved for $z\theta$, the fractional effective neutralization of the bare charge on the wall by condensed counterions. Designating the solution by θ_0 , we have

$$z\theta_0 = 1 - \frac{\kappa(-\ln \kappa/\ell)}{2\pi z l_B \sigma} \quad (9)$$

The right-hand side is indeed a fraction lying between 0 and 1, if the bare surface density of unit charges σ exceeds a critical value

$$\sigma_{\text{crit}} = \frac{\kappa(-\ln \kappa/\ell)}{2\pi z l_B} \quad (10)$$

Note that the critical surface density vanishes in the limit as $C \rightarrow 0$, so the wall condenses all of its counterions in this limit.

The fractional number of condensed counterions θ_0 given by eq 9 is independent of the distance x of the Z-ion from the wall. It has the same value as it would if the Z-ion were absent (as we indicate by the subscript). It therefore satisfies our stipulated requirement for an outer solution. We now show, however, that, although the number of condensed counterions is unperturbed by the presence of the Z-ion in the outer region, the structure of the condensed layer is perturbed. If the left-hand side of the equilibrium condition eq 7 is equal to $-2 \ln \kappa/\ell$, as in eq 8, then so must the right-hand side. Setting the right-hand side of eq 7 equal to $-2 \ln \kappa/\ell$, we find, first of all, that the $-\ln C$ term cancels (since κ^2 is proportional to C) and, second, that the resulting equation may be solved for the condensed layer partition function Q , which takes the form

$$Q = Q_0 e^{-zw(x)} \quad (11)$$

where Q_0 is the internal partition function when the Z-ion is absent

$$Q_0 = 4\pi e \theta_0 z \bar{z} \left(\frac{\nu + \bar{\nu}}{\gamma \nu} \right) l_B^2 \quad (12)$$

with e being the base of the natural logarithm and the barred quantities pertaining to the co-ion. This expression for Q is what we meant by stating that the Z-ion perturbs the structure of the condensed layer; the exponential factor changes its internal free energy.

Let us try to give some physical insight into this formula for Q . The Debye–Hückel interaction $w(x)$ between the wall and the oppositely charged Z-ion is a negative quantity. The valence z of the counterions is unsigned (it is the absolute value of the signed valence). Therefore, $Q > Q_0$. In a simplified model, the partition function Q can be conceived as the local volume of

the condensed layer. In this interpretation, the presence of the Z-ion, with its charge of the same sign as the counterions, allows the condensed layer to become more diffusional, increasing the entropy of the system, and thus enhancing the attraction of the Z-ion toward the wall.

The equilibrated values of θ and Q may be substituted into the various components of G to obtain the minimized free energy of interaction $G(x)$ between the wall and the Z-ion as a function of the distance x between the two. We find that $G(x)$ consists of terms proportional to Z that depend on x and vanish at $x = \infty$ and constant terms independent of either Z or x . The latter give the value of G_∞ when the Z-ion is absent, $Z = 0$, or at infinity. We designate by $\Delta G(x)$ the terms that depend on x . Then, $\Delta G(x) = G(x) - G_\infty$, and therefore equals the work required to move the Z-ion from ∞ to x . In other words, $\Delta G(x)$ is the potential of mean force of the Z-ion at distance x from the wall. We label it $\Delta G_{\text{outer}}(x)$, since it is what we have called the outer solution.

For the purposes of interpretation, we momentarily stop at an intermediate step in the indicated calculations

$$\Delta G_{\text{outer}}(x) = (1 - z\theta_0)Nw(x) + z\theta_0 Nw(x) \quad (13)$$

Referring to eq 2 for $w(x)$, we see that the first term is the Debye–Hückel potential as reduced by an effective wall charge lower than the bare charge because of counterion condensation. This term is what we might expect for the potential $\Delta G(x)$ in the range of distances x outside the condensed layer, which is what we have purported to be calculating. However, there is a second term that cancels a crucial part of the first to give the final result

$$\Delta G_{\text{outer}}(x) = Nw(x) \quad (14)$$

This final result for the outer solution is certainly very simple, but it might also be said to be unexpected. The potential of mean force between the Z-ion and wall in the outer region turns out to equal the bare Debye–Hückel potential. How can this be, given that the Z-ion is positioned outside the layer of counterions condensed on the wall? Mathematically, it is because the second term in the intermediate result eq 13 cancels the part of the first term that lowers the bare charge on the wall by the amount of charge in the condensed layer. The origin of this second term is the exponential factor in eq 11 for the condensed layer partition function Q . When the Z-ion approaches the wall, its attraction to the wall is weakened by the condensed counterions, which decrease the electric field projected by the bare surface charge. However, the approach of the Z-ion also allows the condensed layer to relax, providing a compensating entropic strengthening of the attraction.

We proceed to find another solution to the equilibrium condition, an “inner” one characterized by the stipulation that the Z-ion is so close to the wall that it can replace some of the condensed counterions, which are then released to the solution phase. The equilibrium condition eq 6 may be rearranged

$$4\pi z(l_B\sigma/\kappa)(1 - z\theta) + zw(x) = -\ln C - \ln Q + \ln(\theta/\gamma\nu) + 1 \quad (15)$$

This equation is only a rearrangement of eq 6. It makes no changes in the equilibrium condition. It differs from the rearrangement for the purposes of finding the outer solution, eq 7, only in that the term $zw(x)$ is brought from the right-hand side to the left-hand side.

To get the inner solution, we continuously adjust the surface density σ such that the left-hand side of eq 15 diverges like $-\ln C$ as $C \rightarrow 0$

$$4\pi z(l_B \sigma / \kappa)(1 - z\theta) + zw(x) = -2 \ln \kappa / \quad (16)$$

or, with use of the explicit formula for $w(x)$ from eq 2,

$$4\pi z(l_B \sigma / \kappa) \left[(1 - z\theta) - \frac{Z}{N} e^{-\kappa x} \right] = -2 \ln \kappa / \quad (17)$$

Solving for θ , we get

$$N\theta = N\theta_0 - \frac{Z}{z} e^{-\kappa x} \quad (18)$$

where θ_0 is the value in the absence of the Z-ion, explicitly given in eq 9. Equation 18 states that, in the presence of the Z-ion at x , $(Z/z)e^{-\kappa x}$ counterions are released from the condensed layer.

Since the left-hand side of eq 15 has been set to $-2 \ln \kappa /$, the same must be done to the right-hand side. The $-\ln C$ term cancels, and the solution for Q emerges, $Q = Q_0(\theta/\theta_0)$, where θ is the equilibrium value from eq 18. Since $\theta < \theta_0$, the interpretation would be that the condensed counterions (the ones that have not been released) retract from the Z-ion, becoming more tightly bound. With the equilibrium values of θ and Q thus found, the inner solution for the potential of mean force may be calculated

$$\Delta G_{\text{inner}}(x) = 2(Z/z)e^{-\kappa x} \ln(\kappa /) \quad (19)$$

III. Interpretation of the Solutions

We have found two distinct solutions, eqs 14 and 19, for the potential of mean force of an ion interacting with an oppositely charged wall. Although we have called them “outer” and “inner”, both solutions are smooth functions in the entire range of distances from $x = 0$ out to infinity, as plotted in Figure 1 for a particular numerical example (the values of the parameters match the conditions of the early molecular dynamics simulation of Pandit et al.).²⁰ Note that the outer solution lies below the inner solution.

We have checked by inspection of $\partial^2 G / \partial \theta^2$ that both solutions represent free energy minima. For a fixed distance x , can these two minima exist together? In other words, are there two states between which the system fluctuates with fractional occupancy given by a Boltzmann distribution? The answer is no. If there are two values of θ_{min} for a given x , then there must be an unstable equilibrium characterized by a value of θ_{max} lying between the minimizing θ values. This θ_{max} would be another solution of the equilibrium condition $\partial G / \partial \theta = 0$. However, there

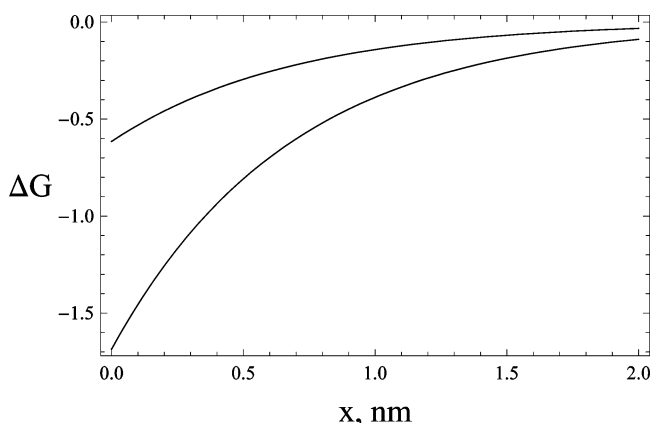


Figure 1. The outer (lower curve) and inner (upper curve) solutions for the potential of mean force ΔG in units of $k_B T$ as a function of distance x of the Z-ion from the wall at $x = 0$. $Z = z = 1$, $l_B = 0.71$ nm, $\kappa^{-1} = 0.68$ nm, $\ell = 5$ nm, $\sigma = 1/(3.6 \text{ nm}^2)$.

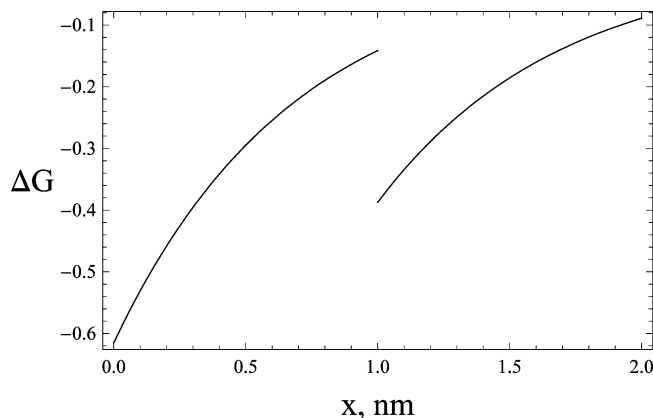


Figure 2. Same as Figure 1 but showing the jump from the outer to the inner energy trajectory. The plot is for visual purposes only, since the location of the jump was arbitrarily chosen (see text).

is no other solution. To get the outer equilibrium, we shifted $w(x)$ in eq 6 to the right-hand side. For the inner equilibrium, we allowed $w(x)$ to remain on the left-hand side. There is no other place for $w(x)$ to go. We conclude that the two minimizing solutions, as implied by their names, pertain to distinct ranges of x . As the Z-ion approaches from infinity, its initial trajectory is along the outer potential of mean force. On closer approach, it transitions to the inner potential.

To delve further, we observe an interesting relationship between the outer and inner solutions. For any fixed x ,

$$\Delta G_{\text{outer}}(x) = \frac{\sigma}{\sigma_{\text{crit}}} \Delta G_{\text{inner}}(x) \quad (20)$$

This equation follows easily from the formulas for the two solutions, using the explicit expression for $w(x)$ from eq 2 and the expression for σ_{crit} from eq 10 (the mutuality of the critical condition for both solutions holds to within a $O(N^{-1})$ term, which is negligible since $N \rightarrow \infty$). Both $\Delta G_{\text{outer}}(x)$ and $\Delta G_{\text{inner}}(x)$ are negative quantities for any x , and since $\sigma > \sigma_{\text{crit}}$, the outer potential is more negative than the inner. Furthermore, since the ranges of validity of the two potentials are disjoint, there must be a jump of magnitude $\sigma/\sigma_{\text{crit}}$ between them as x decreases toward the wall. The only other possibility is a progressive transition between the two solutions. This possibility would require the existence of a third solution to bridge between the inner and outer solutions. However, the existence of a third solution can be ruled out, as discussed in the second paragraph of this section.

In Figure 2, we give an illustration with an arbitrarily chosen location for the jump. Where in fact does the jump occur? We can think of no reason for occurrence of a jump at any value $x > 0$. Nothing in the system, either physical or mathematical, suggests a discontinuity away from the wall. We conclude that the jump occurs at the wall itself, $x = 0$. For the numerical example chosen, Figure 1 shows a significant jump, $\sim 1.1 k_B T$, at the wall.

Here, then, is the picture that has emerged. The pointlike condensed counterions are located *on* the wall, that is, at the plane $x = 0$, where they congregate with the bare wall charge. When a Z-ion with charge opposite to the bare wall charge approaches from infinity, the electrostatic free energy of the system decreases in accordance with $\Delta G_{\text{outer}}(x)$ all the way up to the wall. When the pointlike Z-ion reaches the wall, it penetrates the condensed layer. The system responds with an abrupt increase of electrostatic free energy and a release of Z/z condensed counterions, maintaining the effective charge density

on the wall at the value $e\sigma_{\text{crit}}$. If $Z = z$, then the Z -ion is itself a counterion, and the statement becomes that if a counterion is added to the condensed layer, another counterion leaves. The interpretation of the free energy jump at the wall is that, when the Z -ion touches the like-charged condensed layer at $x = 0$, it is strongly repelled. In other words, the Z -ion is not smoothly attracted to the oppositely charged wall. On approach, it is attracted toward the wall, but before it penetrates the condensed layer of counterions on the wall, it meets a repulsive barrier.

IV. Discussion

The picture we have described in the previous section has obvious deficiencies when viewed at a molecular level. All of the interesting “action” occurs when the distance x between the Z -ion and the wall is equal to zero, the value purported by the underlying continuum model to be the location of the surface of the wall. The condensed counterions are located on the wall at $x = 0$. The repulsive barrier encountered by the Z -ion is represented as a free energy jump at $x = 0$. As the Z -ion penetrates the condensed layer, releasing Z monovalent counterions, it moves from $x = 0^+$ to $x = 0^-$. If any physical sense is to be gathered from a model so abstract, we must discuss the meaning on a molecular level of the statement “ $x = 0$ ”, and for that, the indeterminate fixed length l must be given substance.

We introduced the quantity $-\ln \kappa^2/2$ in order to remove the counterion dissociation divergence $-\ln C$ from the equilibrium condition. As such, the resulting formulas are asymptotically valid to lowest order, with κl being the small dimensionless quantity. The length l must be much less than the screening length κ^{-1} but is otherwise indeterminate, since all terms of the form $-\ln \kappa l$ are asymptotically equal. In a previous paper, we chose $l = l_B$, the Bjerrum length, reasoning that no other length was present among the parameters of the model. However, there is another length implied by the model, namely, the thickness of the condensation layer. Clearly, in the model, a condition for the existence, indeed the meaning, of a condensation layer distinct from the more diffuse Debye ion cloud is that its thickness l is much less than a screening length. This choice for l is better motivated than the arbitrary choice of the Bjerrum length.

For a real system, then, we interpret the location $x = 0$ as signifying the narrow but nonzero width Δx that defines the wall surface on the level of its molecular roughness. For example, a glass surface is mesoporous; Δx is plausibly taken as the average depth of the pores. The surface of a phospholipid bilayer can be envisaged as the width Δx of its bounding polar headgroup regions, which are permeated by water molecules and small ions.⁵ The parameter l might then be taken as equal to Δx , and the condensed counterions could be described as distributed, not necessarily uniformly, within a thin layer of thickness $\Delta x = l$, where they come in contact with the polar groups and water molecules that define the hydrated headgroup interface. With this interpretation of l , we can try to suggest a qualitative connection with an interesting feature revealed in molecular dynamics simulations of phospholipid bilayers.

Proceeding outward in either direction from the central plane of a phospholipid bilayer, one first traverses an “oily” region consisting of hydrocarbon chains partially stretched and roughly in parallel, and then a polar “headgroup” region, about 1 nm in width, before entering the bulk aqueous phase outside the bilayer.⁵ The headgroup region is permeable to water and ions, and as discussed in the previous paragraph, we interpret the length l as representing its thickness, $l \approx 1$ nm. There are various species of phospholipids, but one of them has a

negatively charged serine carboxylate group at its outer periphery, rendering the interfaces of bilayers that contain it negatively charged. In an earlier simulation of these charged bilayers, Na^+ counterions exhibited two peaks of density.²¹ Both Na^+ and K^+ counterions were also seen distributed in this way in a more recent simulation.²² It is this double peak that we want to discuss briefly in the light of the counterion condensation results of the present paper. Because the value $l \approx 1$ nm implies that κl is a small quantity only for salt concentrations substantially less than used in the simulations, we can engage in no more than qualitative remarks concerning two points of view that could be taken in interpreting the double peak of counterion density.

The two peaks of counterion density could be interpreted simply as indicating the two preferred locations of counterions that are adsorbed into the headgroup region. In fact, the inner of the two peaks coincides with the density peak of the electronegative carbonyl oxygens, a structural feature of all of the phospholipids, while the outer peak is close to the density peak of the negatively charged carboxylate groups.²² Another, partially overlapping, possibility is that the inner peak can be identified with condensed counterions, and the outer peak with a Debye–Hückel-like layer outside the headgroup region. That is, the observation of two counterion peaks could reflect the inner and outer solutions to the theoretical problem posed in this paper. It is worth discussing this possibility in slightly more detail.

In the idealized model, when a counterion crosses the charged plane at $x = 0$, it becomes condensed. In a more realistic system, as studied in the simulations, the condensed counterions would preferentially seek locations of lowest free energy, for example, the carbonyl oxygen subregion of lipid headgroups or the negatively charged phosphate moiety of the phosphate–choline zwitterionic pair.

The outer counterion peak, as observed in the simulation,²² is actually located just outside the density peak for the negatively charged serine carboxylate group. In turn, the serine carboxylate is close to the outer edge of the headgroup region. Close inspection of the density profiles reported in Figure 5 of ref 22 shows that the outer counterion density peak nearly coincides with the distance from the bilayer center where water density attains its bulk value and lipid atom densities fall to zero. In other words, the outer counterion peak is located just outside the bilayer. The corresponding statement about the theoretical model is that the outer solution extends right up to the plane $x = 0$.

Although there is this possible connection of the theory with all-atom computer simulations, no present experimental evidence of which we are aware exists to support the prediction of two coexisting counterion populations—condensed and diffuse—for systems of charged planar walls. We did mention ref 18 in the Introduction, which provides confirming data for spherical particles of large radius, and to the extent that a particle with large radius can be viewed as a model for a wall with infinite radius of curvature, these data can be construed as at least suggesting extrapolation to planes. However, for actual planar surfaces (for example, glass walls, mica coated with varying amounts of a charged substrate, or lipid bilayers), there are no direct experimental data. Confirming data for polyelectrolytes are copious, however.^{15,19} The variety of laboratory methods and designs of experiments used for this purpose have been reviewed in ref 15. Possibly some ideas for appropriate laboratory work on walls could emerge from what has already been done with polyelectrolytes.

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