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R. J. Nap, M. Tagliazucchi, and I. Szleifer[a)]
Department of Biomedical Engineering, Department of Chemistry, and Chemistry of Life Processes Institute, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3100, USA

This work addresses the effect of the Born self-energy contribution in the modeling of the structural and thermodynamical properties of weak polyelectrolytes confined to planar and curved surfaces. The theoretical framework is based on a theory that explicitly includes the conformations, size, shape, and charge distribution of all molecular species and considers the acid-base equilibrium of the weak polyelectrolyte. Namely, the degree of charge in the polymers is not imposed but it is a local varying property that results from the minimization of the total free energy. Inclusion of the dielectric properties of the polyelectrolyte is important as the environment of a polymer layer is very different from that in the adjacent aqueous solution. The main effect of the Born energy contribution on the molecular organization of an end-grafted weak polyacid layer is uncharging the weak acid (or basic) groups and consequently decreasing the concentration of mobile ions within the layer. The magnitude of the effect increases with polymer density and, in the case of the average degree of charge, it is qualitatively equivalent to a small shift in the equilibrium constant for the acid-base equilibrium of the weak polyelectrolyte monomers. The degree of charge is established by the competition between electrostatic interactions, the polymer conformational entropy, the excluded volume interactions, the translational entropy of the counterions and the acid-base chemical equilibrium. Consideration of the Born energy introduces an additional energetic penalty to the presence of charged groups in the polyelectrolyte layer, whose effect is mitigated by down-regulating the amount of charge, i.e., by shifting the local-acid base equilibrium towards its uncharged state. Shifting of the local acid-base equilibrium and its effect on the properties of the polyelectrolyte layer, without considering the Born energy, have been theoretically predicted previously. Account of the Born energy leads to systematic, but in general small, corrections to earlier theoretical predictions describing the behavior of weak polyelectrolyte layers. However, polyelectrolyte uncharging results in a decrease in the concentration of counterions and inclusion of the Born Energy can result in a substantial decrease of the counterion concentration. The effect of considering the Born energy contribution is explored for end-grafted weak polyelectrolyte layers by calculating experimental observables which are known to depend on the presence of charges within the polyelectrolyte layer: inclusion of the Born energy contribution leads to a decrease in the capacitance of polyelectrolyte-modified electrodes, a decrease of conductivity of polyelectrolyte-modified nanopores and an increase in the repulsion exerted by a planar polyelectrolyte layer confined by an opposing wall. © *2014 AIP Publishing LLC*.
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I. INTRODUCTION

Soft materials confined to planar and curved interfaces behave very differently than those in bulk.[1–3] Molecular confinement leads to an increased local density which exacerbates the competition between different physical and chemical interactions and leads to emerging and interesting phenomena. A well-known example is charge regulation by acid-base equilibrium, the process by which a chemical equilibrium involving charging (or uncharging) of monomers is shifted in order to reduce the net charge of the system and thus globally optimize the different competing interactions.[1,4,5]

The dielectric environment of confined soft materials is not only very different from bulk, but it is also highly inhomogeneous. Thus, it is important to understand how the dielectric properties couple to the different physical and chemical interactions and affect the organization of the system. For instance, a dielectric medium stabilizes charges with respect to vacuum by an energy amount known as the Born or self-energy. In this paper, we explore, for the first time to the best of our knowledge, the effect of a non-constant Born energy on the structure, composition, and electrochemical properties of an end-grafted weak polyelectrolyte layer using a molecular theory.

End-tethered weak polyelectrolyte layers have been studied both experimentally and theoretically. There has been considerable theoretical effort to elucidate their behavior. These efforts include numerical and analytical self-consistent field theory, scaling theory, and computer simulations.[1,4,6–14] For example, Fleer and co-workers used lattice self-consistent

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a)Electronic mail: igalsz@northwestern.edu

field theory, also known as Scheutjens-Fleer theory,[6–8] to numerically investigate the behavior of tethered weak polyelectrolytes layers, while Zhulina *et al.* and Lyatskaya *et al.* applied analytical self-consistent field approaches.[9–11,13] From these seminal works and subsequent studies emerged a general understanding that the behavior of weak polyelectrolyte layers is governed by a local acid-base equilibrium. For a polyacid, the local acid-base equilibrium shifts towards the uncharged or protonated state of the acid with increasing polymer density and decreasing salt concentrations. Invariably, researchers have assumed a constant dielectric background and neglected the effects of varying dielectric constant and Born self-energy. Noted exception are Refs. 15 and 16. Here, we include the Born energy into a molecular theoretical description previously used to study polymer at interphases.[17]

The inclusion of the Born energy contribution shifts the acid-base equilibrium of the grafted weak polyelectrolytes and decreases the effective concentration of ions and charged groups within the layer.

Taking into account the Born energy leads to a systematic, but generally small, correction to the predictions of earlier theories describing the behavior of weak polyelectrolyte layers. However, the correction to the effective concentration of ions and charged groups within the layer can be very large at high grafting densities.

We also discuss specific examples where the inclusion of the Born energy contribution is translated into differences in experimental observables: the capacitance of polyelectrolyte-modified electrodes, the ion-conductivity of polyelectrolyte modified nanopores, and the interaction force between a polyelectrolyte modified planar surface and an opposing wall.

Previously, the theory used in this work was applied to investigate the thermodynamic and structural properties of a variety of tethered weak polyelectrolyte systems.[15,18–20] We refer to the theoretical approach as molecular theory since its formulation explicitly includes molecular details of all the components in the systems studied. The predictions of the theory have been found to be in excellent agreement with experimental observations such as in the height of weak-polyelectrolytes (polyacrylic-acid) end-tethered to a planar surface,[21,22] the conductivity of nanochannels modified by weak polyelectrolytes,[23] and charge regulation of acid-coated nanoparticles.[24] The key aspect of that molecular approach is that it accounts explicitly for the conformations of the polymer chains, size, and charge distribution of every molecular species in the system. Moreover, the theory does not assume the state of the charge of the acid (or basic) groups, but it rather predicts the non-homogenous state of charge. Within the framework of the molecular theory,[15] we also studied the effect of having a varying dielectric medium, i.e., varying dielectric constant, on the charge regulation of the weak polyelectrolytes. As recently demonstrated by Wang,[25,26] proper consideration of a varying dielectric constant, that is having a non-uniform media, also necessitates the inclusion of a non-uniform Born or self-energy in the free energy functional. In previous work, we neglected the change in self-energy. We present here, in the context of the molecular theory, both the effect of having a varying dielectric constant and a varying self-energy on the properties of weak polyelectrolyte layers.

The paper is organized as follows. In Sec. II, we derive the molecular theory for end-tethered weak polyelectrolytes that includes the Born self-energy. This is followed by a presentation and discussion of the effect of the Born energy contribution on the behavior of weak polyelectrolyte layers in Sec. III along with a discussion of relevant systems for which the effect of Born energy is important. Finally, Sec. IV is devoted to concluding remarks.

II. THEORETICAL APPROACH

A. Self-energy

The electrostatic free energy change for transferring an ion from vacuum to an uniform dielectric media is, following Born,[27,28] given by

$$\Delta G^B = \frac{q^2}{8\pi\varepsilon_0 a}\left(\frac{1}{\varepsilon}-1\right),\tag{1}$$

here a corresponds to the radius of the ion and q to its charge, ε is the relative dielectric constant of the medium, and ε_0 is the electric constant or permittivity of free space. The constant term has no thermodynamic consequences and therefore we do not include it hereafter and write the Born contribution to the free energy of an ion as follows:

$$u^B = \frac{q^2}{8\pi\varepsilon_0\varepsilon a}.\tag{2}$$

The above free energy is sometimes referred to as the solvation energy of the ion. We will denote it as the Born or self-energy and reserve the more general term solvation energy to include also contributions due to compositional changes and reorganization of the surrounding molecules of the medium (see also Ref. 25).

Assuming that the medium is inhomogeneous, then the dielectric function is position dependent. Hence the self-energy will depend on the location of the charge. Therefore, we propose to write the total electrostatic self-energy of all charges present in an inhomogeneous medium as follows:[25,26]

$$u^B = \sum_i \int dz\, u_i^B(z)\rho_i(z) = \sum_i \int dz\, \frac{q^2}{8\pi\varepsilon_0\varepsilon(z)a_i}\rho_i(z),\tag{3}$$

where $u_i^B(z)$ is the position dependent self- or Born energy and $\rho_i(z)$ is the density of charged species i at z. To describe the dielectric medium we need to employ a constitutive equation. We will model the dielectric function as the average of the dielectric functions of the components of the system, weighted by their respective local volume fractions,

$$\varepsilon(z) = \sum_i \varepsilon_i \phi_i(z),\tag{4}$$

$$= \varepsilon_p\langle\phi_p(z)\rangle + \varepsilon_w(1-\langle\phi_p(z)\rangle).\tag{5}$$

Here $\phi_i(z)$ and $\langle\phi_p(z)\rangle$ correspond to the volume fraction of species i and the polymer volume fraction, respectively. The effect of salt ions on the dielectric properties of an aqueous solution are only noticeable for salt concentrations in the

molar range.[29,30] Because we are primarily interested in salt concentrations in the range around physiological conditions ($c \sim 100$ mM), we will assume that the ions have the same dielectric constant as the solvent. In the calculations the relative dielectric constant of the polymers is equal to $\varepsilon_p = 2$ and the aqueous solution has a value of $\epsilon_w = 78.5$.

B. Molecular theory: Weak polyelectrolytes

A schematic representation of weak polyelectrolytes end-tethered to a planar surface is shown in Figure 1. The free energy per unit area for the end-tethered weak polyelectrolytes is given by

$$f = \frac{\beta F}{A} = \sigma_p \sum_\alpha P(\alpha) \ln P(\alpha) + \int dz \, \rho_w(z)(\ln \rho_w(z)v_w - 1)$$

$$+ \sum_{i=\{+,-\}} \int dz \, \rho_i(z)(\ln \rho_i(z)v_w - 1) + \sum_{i=\{H^+, OH^-\}} \int dz \, \rho_i(z)\left(\ln \rho_i(z)v_w - 1 + \beta\bar{\mu}_i^\ominus\right)$$

$$+ \int dz \, \langle \rho_p(z) \rangle \left[f(z)\left(\ln f(z) + \beta\bar{\mu}_{A^-}^\ominus\right) + (1 - f(z))\left(\ln(1 - f(z)) + \beta\mu_{AH}^\ominus\right) \right]$$

$$+ \sum_{i=\{+,-,H^+,OH^-\}} \beta \int dz \, u_i^B(z)\rho_i(z) + \beta \int dz \, u_p^B(z)f(z)\langle \rho_p(z) \rangle$$

$$+ \beta \int dz \left(\langle \rho_q(z) \rangle \psi(z) - \frac{1}{2}\varepsilon_0\varepsilon(z)\left(\frac{d\psi(z)}{dz}\right)^2 \right) + \beta\sigma_q\psi(0)$$

$$+ \frac{1}{2}\beta \iint dz dz' \, \chi(|z - z'|)\langle \rho_p(z) \rangle\langle \rho_p(z') \rangle, \tag{6}$$

where $\beta = 1/k_B T$ is the inverse temperature. The first term describes the conformational entropy of the tethered polymers. $P(\alpha)$ is the probability of finding a tethered polymer chain in conformation α and $\sigma_p = N_p/A$ is the number of tethered polymer chains per unit area. The thermodynamic and structural properties of the polymer can be calculated from the probability distribution function. For instance, the average volume fraction of the polymers at position z is given by

$$\langle \phi_p(z) \rangle = \sigma_p \sum_\alpha P(\alpha)n_p(\alpha; z)v_p. \tag{7}$$

Here $n_p(\alpha; z)dz$ is the number of polymer segments within the element $[z, z + dz]$ belonging to polymer conformation α. v_p denotes the volume of one polymer segment.

The second term in the free energy expression represents the mixing (translational) entropy of the solvent and $\rho_w(r, z)$ is the number density of the water (solvent) and v_w is its volume. The volume fraction of the water at z is given by $\phi_w(z) = \rho_w(z)v_w$. The next two contributions of the free energy describe the mixing (translation) entropy and chemical potential of the mobile ionic species.

The fifth term in the free energy describes the free energy associated with the chemical acid-base equilibrium

$$AH \leftrightharpoons A^- + H^+, \tag{8}$$

where $f(z)$ corresponds to the fraction of charged monomers and $\langle \rho_p(z) \rangle = \langle \phi_p(z) \rangle/v_p$ is the polymer density both at z. The first and third terms within the integral describe the entropy of the deprotonated charged state (A^-) and protonated state (AH), respectively. The second and fourth terms within the integral correspond to the standard chemical potential of the charged and uncharged state, respectively. Special attention needs to be paid to the definition of $\bar{\mu}_{A^-}^\ominus$ and $\bar{\mu}_{H^+}^\ominus$. They denote the standard chemical potential for the charged polymer monomer and the proton and do *not* explicitly include the self-energy. The total standard chemical potential of the charged monomer and proton in bulk medium (i.e., the standard free energy of formation in the solvent) also has a self-energy contribution: $\mu_i^\ominus = \bar{\mu}_i^\ominus + u_i^B$. A bar is used to differentiate these contributions in the chemical potential from each other. The reason for this separation of the standard chemical
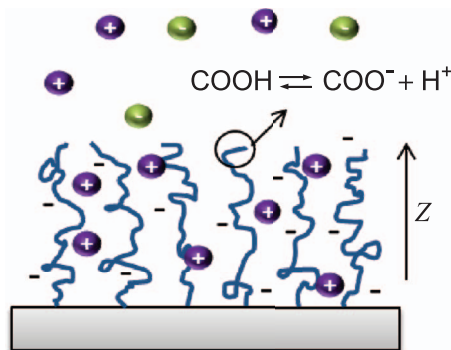

FIG. 1. Schematic representation of a weak polyelectrolyte layer end-tethered to a planar surface, including the coordinate system used.

potentials will become apparent below when discussing the free energy minimization.

The sixth and seventh terms in the free energy functional represent the self-energy contribution.[31]

The next two terms in Eq. (6) describe the electrostatic contribution to the free energy functional.[32–34] Here $\psi(z)$ corresponds to the electrostatic potential at position z. $\langle\rho_q(z)\rangle$ and σ_q are the charge density at z and the surface charge density, respectively. The local charge density equals

$$\langle\rho_q(z)\rangle = -ef(z)\langle\rho_p(z)\rangle + e\rho_+(z) - e\rho_-(z)$$
$$+ e\rho_{H^+}(z) - e\rho_{OH^-}(z), \tag{9}$$

where e is the elementary charge.

Non-electrostatic van der Waals interactions are represented by the last term of the free energy functional. It describes the solvent quality. Here $\chi(|\vec{r} - \vec{r}'|) = -\varepsilon_{VdW}\ell^6/(|\vec{r} - \vec{r}'|)^6$ is an attractive van der Waals potential, where ℓ denotes the segment length of the polymer. The variable ε_{VdW} corresponds to the strength of the van der Waals interactions. For good solvent condition: $\chi(|\vec{r} - \vec{r}'|) = 0$.

The repulsive interactions in the theory are modeled as excluded volume interactions. The intrachain interactions are considered exactly during chain conformation generation. The intermolecular excluded volume interactions are accounted for by assuming that the system is incompressible at every position

$$\langle\phi_p(z)\rangle + \phi_w(z) + \phi_+(z) + \phi_-(z) + \phi_{H^+}(z) + \phi_{OH^-}(z) = 1. \tag{10}$$

These volume constraints are enforced through the introduction of the Lagrange multipliers $\pi(z)$. Note that the volume fraction of each species explicitly includes its shape, size, and in the case of the polymers a sum over the possible conformations.

The free energy is minimized with respect to the $P(\alpha)$, $\rho_i(z)$, and $f(z)$, and varied with respect to the electrostatic potential $\psi(z)$ under the constraints of incompressibility and the fact the system is in contact with a bath of cations, anions, protons, and hydroxyl ions. The proper thermodynamic potential becomes

$$w = f - \sum_{i=\{w,+,-,OH^-\}} \beta\mu_i \int dz\, \rho_i(z)$$
$$- \beta\mu_{H^+}\left(\int dz\, \rho_{H^+}(z) + (1 - f(z))\langle\rho_p(z)\rangle\right)$$
$$+ \beta\int dz\pi(z)\left(\langle\phi_p(z)\rangle + \sum_{i=\{w,+,-,H^+,OH^-\}}\phi_i(z) - 1\right). \tag{11}$$

The probability distribution function becomes

$$P(\alpha) = \frac{1}{q}\exp\left[-\beta\int dz\, n(\alpha;z)\left(\pi(z)v_p + \psi(z)(-e) + \frac{1}{\beta}\ln f(z) - \frac{1}{2}\varepsilon_0\frac{\delta\varepsilon(z)}{\delta\rho_p(z)}\left(\frac{d\psi(z)}{dz}\right)^2\right)\right]$$
$$\times \exp\left[-\beta\iint dz dz'\, n(\alpha;z)\chi(|z-z'|)\langle\rho_p(z')\rangle\right]$$
$$\times \exp\left[-\beta\int dz\, n(\alpha;z)\left(u_p^B(z) - {\sum_i}' u_i^B(z)\rho_i(z)\frac{\delta\ln\varepsilon(z)}{\delta\rho_p(z)}\right)\right]. \tag{12}$$

q is a normalization factor ensuring that $\sum_\alpha P_i(\alpha) = 1$. The first term in the exponential results from the repulsive excluded volume interactions that a polymer in conformation α experiences. The second and fourth terms include a purely electrostatic contribution whereas the third term is an entropy like term associated with the degree of charging of the chargeable group. The fifth term is related to the van der Waals interaction among the monomers. The last two terms originate from the coupling of the polymer density to the Born self-energy. In the final term of the probability distribution function, the summation over i runs over all *charged* species, i.e., the co- and counter ions, protons, hydroxyl ions, and the charged groups in the polyelectrolyte (thus $i = p$ involves $f(z)\langle\rho_p(z)\rangle$). This fact is indicated here and in the following equations through the prime in the summation. It is important to emphasize that the second, third, and fourth terms in the probability distribution function appear after algebraic rear-

rangement. The terms arising from the electrostatic interactions and chemical equilibrium are combined with the equation for the fraction of charged monomers, Eq. (18), to yield the second through fourth terms in the probability distribution function.[15]

The local density of the free ions is given by

$$\rho_i(z)v_w = \exp\left(\beta(\mu_i - \bar{\mu}_i^\ominus) - \beta\pi(z)v_i - \beta\psi(z)z_i e\right)$$
$$\times \exp\left(\frac{1}{2}\beta\varepsilon_0\frac{\delta\varepsilon(z)}{\delta\rho_i(z)}\left(\frac{d\psi(z)}{dz}\right)^2\right)$$
$$\times \exp\left(-\beta u_i^B(z) + \beta{\sum_k}' u_k^B(z)\rho_k(z)\frac{\delta\ln\varepsilon(z)}{\delta\rho_i(z)}\right). \tag{13}$$

The expression for the local density of the solvent is given by

$$\rho_w(z)v_w = \exp\left(-\beta\pi(z)v_w + \frac{1}{2}\beta\varepsilon_0 \frac{\delta\varepsilon(z)}{\delta\rho_w(z)}\left(\frac{d\psi(z)}{dz}\right)^2\right)$$
$$\times \exp\left(\beta\sum_i' u_i^B(z)\rho_i(z)\frac{\delta\ln\varepsilon(z)}{\delta\rho_w(z)}\right). \qquad (14)$$

For the special case where the dielectric function only explicitly depends on the polymer density (Eq. (5)), the expression for the solvent density simplifies to

$$\phi_w(z) = \rho_w(z)v_w = \exp(-\beta\pi(z)v_w). \qquad (15)$$

Similarly, the ion local density becomes

$$\rho_i(z)v_w = \exp\left(\beta\mu_i - \beta\bar\mu_i^\ominus - \beta u_i^B(z) - \beta\pi(z)v_i - \beta\psi(z)z_ie\right). \qquad (16)$$

It is important to mention that the incompressibility constraint reduces the number of thermodynamical independent variables by one. Therefore, the chemical potentials, μ_i are in reality exchange chemical potentials, which we define as the difference between the chemical potential of the species i and that of water. In a similar fashion charge neutrality and the water self-dissociation equilibrium reduce the number of thermodynamic independent variables further. The values of the exchange chemical potential of the remaining species are readily expressed by relating them to their (known) bulk concentrations: $\rho_i^{bulk}v_w = \exp(\beta\mu_i - \beta\bar\mu_i^\ominus - \beta u_i^B - \beta\pi^{bulk}v_i)$.

Functional variation of the free energy with respect to the electrostatic potential yields the Poisson equation and its boundary conditions

$$\varepsilon_0\frac{d}{dz}\left(\varepsilon(z)\frac{d\psi(z)}{dz}\right) = -\langle\rho_q(z)\rangle \qquad -\varepsilon_0\varepsilon(z)\frac{d\psi(z)}{dz}\bigg|_{z=0} = \sigma_q$$
$$\lim_{z\to\infty}\psi(z) = 0. \qquad (17)$$

In the free energy functional, the term $\varepsilon_0\varepsilon(z)(\frac{d\psi(z)}{dz})^2$ corresponds to the dielectric energy, but it does not fully capture the Born energy contribution, because $\psi(z)$ is a mean-field electrostatic potential. Due to the mean-field approximation, the electrostatic potential in the Poisson equation is replaced with the thermodynamically averaged electrostatic potential. For instance, the activity of a charged particle inserted in an otherwise neutral system will not capture or experience the effect of the varying dielectric constant. In order to capture the Born-self energy, we therefore heuristically introduced it in Eq. (3). Introduction of the Born self-energy term can be made precise for the case of electrolyte solutions. As recently derived by Wang in Ref. 26 by means of a field-theoretical expansion: consideration of a varying dielectric function results in the appearance, to first order, of Born self-energy terms in the effective free energy functional describing the electrolyte solution.

Minimizing the free energy functional with respect to the fraction of charged monomers leads to

$$\frac{f(z)}{1 - f(z)} = K_a^\ominus e^{-\beta\Delta G_s(z)}\frac{e^{-\beta\pi(z)v_{H^+}}}{\rho_{H^+}(z)v_{H^+}}, \qquad (18)$$

where $K_a^\ominus = e^{-\beta\Delta G_a^\ominus}$ is the chemical equilibrium constant and $\Delta G_a^\ominus$ is the standard free energy change of the reaction $AH \rightleftharpoons A^- + H^+$, and given by $\Delta G_a^\ominus = \mu_{A^-}^\ominus + \mu_{H^+}^\ominus - \mu_{AH}^\ominus$. The standard free energy change is related to the experimental equilibrium constant $K_a = C\exp(-\beta\Delta G_a^\ominus)$ of a single acid molecule in dilute solution, where C is a constant to be introduced for consistency of units. Observe that the standard chemical potentials, $\mu_{A^-}^\ominus$ and $\mu_{H^+}^\ominus$ also include contributions arising from the Born self-energy. In the equation describing the fraction of charged monomers, (Eq. (18)), $\Delta G_s(z) = \Delta u_p^B(z) + \Delta u_{H^+}^B(z)$, where $\Delta u_i^B(z) = u_i^B(z) - u_i^B$ is the difference between the Born energy of species i at position z and its value in solution. Thus, $\Delta G_s(z)$ is the difference in self-energy of creating a charged polymer monomer and proton pair at position z and in the reference solution. This term is similar to the "dielectric mismatch" term introduced by Muthukumar *et al.* in a theoretically description of counterion condensation to polyelectrolytes.[35–37] The dielectric function of polymers is usually in the range of $\varepsilon_p \in (2, 10)$ whereas water has a higher value of $\epsilon_w = 78.5$. Hence, $\beta\Delta G_s(z)$ will be positive.

The unknowns in Eq. (12) through Eq. (18) are the Lagrange multipliers or lateral pressures, $\pi(z)$, the electrostatic potential, $\psi(z)$, and the polymer volume fraction, $\langle\rho_p(z)\rangle$. Application of the theory requires the evaluation of these variables. This can be accomplished by substituting the expressions of the probability distribution function of chain conformations and the volume fractions of all components into the incompressibility constraints and the Poisson equation. Combining these two equations with the equation for the polymer volume fraction, Eq. (7), results in a set of integro-differential equations whose solution will determine the lateral pressures, electrostatic potential, the degree of protonation, and the volume fraction of the polyelectrolyte, the ions, and the solvent. By discretizing space, the differential equations convert into a set of coupled nonlinear equations, whose solution can be obtained by standard numerical techniques.[38] Details on the discretization procedure and numerical methods can be found in Ref. 15. The inputs required to solve the nonlinear equations are the bulk pH, salt concentration, a set of polymer conformations, the surface coverage of the end-tethered polyelectrolytes, the pK_a of the acidic group, as well as the Born-radii of all charged species, and the volume of all species. Unless stated otherwise, these values are the ones listed below in Table I.

Finally, the chain model we use to generate a representative set of polymer conformations is based of an isoenergetic three-state RIS model with a segment length of $\ell = 0.5\,\text{nm}$. The conformations are generated by a simple sampling Monte Carlo method and all generated

TABLE I. Volume, charge, and Born radii of the various molecular species.

	$v(\text{nm}^3)$	$q(e)$	$a(\text{nm})$
Polymer	0.113	-1	0.3
Water	0.030	0	0.193
H^+/OH^-	0.030	± 1	0.193
$+/-$	0.034	± 1	0.2

conformations are self-avoiding and do not penetrate the tethering surface. In all calculations, we have used a set of 10^6 conformations. Further details on the chain model can be found in Refs. 17 and 39.

III. RESULTS

Here we have chosen a number of representative cases to emphasize and illustrate the effect of the Born energy on structural and thermodynamical properties of planar tethered polyelectrolytes.

A. Structural properties of weak polyelectrolyte layers

First we investigate the effect of inclusion of the Born energy contribution on the density profile and on the degree of charge within a weak polyelectrolyte layer. We shall compare the results to those obtained without considering the Born energy contribution. In order to focus solely on the effect of Born energy, we fix a number of parameters: the polymers have a chain length of 50 segments and the pK_a of the ideal solution of the isolated acid groups is 5, which is comparable to that of a carboxylic acid group, i.e., polyacrylic acid.

Figure 2 shows the polymer volume fraction and the effective dielectric function for different surface coverages (tethered polyelectrolytes per unit area). Increasing the surface grafting density results in an increase of the polymer density (up to 20% volume fraction is occupied by polymer segments). Concomitantly with the increase of the polymer density the dielectric function drops in value to a

similar degree within the polymeric layers, following Eq. (4). The polymer density predicted with the molecular theory with and without the Born energy contribution are indistinguishable on the scale of Fig. 2.

The absence of any significant structural changes is already anticipated based on previous calculations comparing density profiles with and without varying dielectric function[15] and can be explained based upon the behavior of the electrostatic potential and degree of charge, as will be done below. Here it is important to mention that the polymeric layer constitutes, due to the presence of the polymer chains, an environment that has a much smaller dielectric function as compared to an aqueous solution. Consequently, one expects that the local environment of polymer layer will influence and be coupled to the local degree of charge of the acid within the polymer layer.

To characterize the behavior of weak polyelectrolyte layers and to quantify the changes that arise from inclusion of the Born energy, we computed the average degree of charge in a polyacid layer. The average degree of charge is given by

$$\langle f \rangle = \frac{\int dz\, f(z) \langle \rho_p(z) \rangle}{\int dz\, \langle \rho_p(z) \rangle}. \qquad (19)$$

In Figure 3, the average degree of charge as function of pH is shown for a weak tethered polyelectrolyte layer in aqueous solutions of different salt concentration and for polyelectrolyte layers having different surface coverages. For comparison, the solid line labelled "bulk" shows the degree of charge
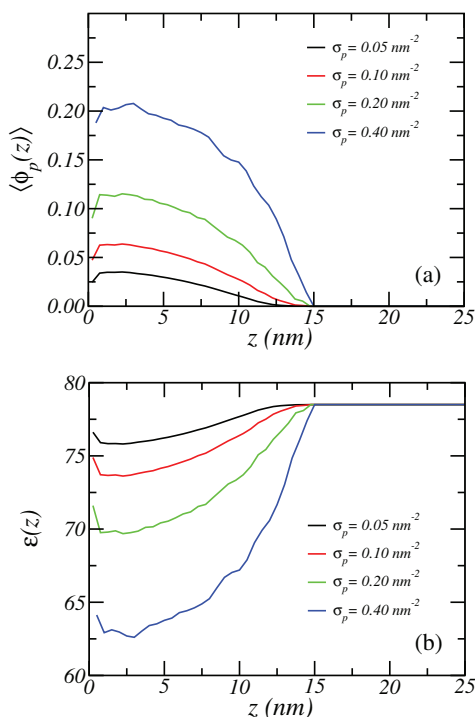

FIG. 2. (a) The polymer volume fraction as function of the distance from the planar grafting surface. (b) The relative dielectric constant as function of the distance from the planar grafting surface. For all cases the number of segments is $n = 50$, the bulk solution $pH = 5$, the $pK_a = 5$, and the salt concentration is $c_s = 100$ mM.
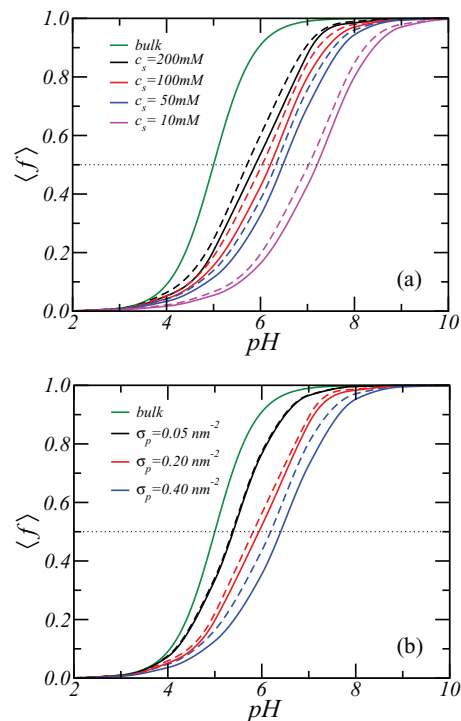

FIG. 3. Average degree of charge as function of bulk pH for (a) various salt concentrations and (b) different surface coverages. In (a), the surface coverage is equal to $\sigma_p = 0.30\ \text{nm}^{-2}$. In (b), the salt concentration is equal to $c_s = 100$ mM. The number of segments is equal to $n = 50$ and $pK_a = 5.0$. The solid lines correspond to the case where the Born energy contribution is included in the free energy. The dashed lines correspond to the case where the Born energy contribution was not included

of a single isolated acid molecule in the bulk solution, which follows the ideal chemical equilibrium equation: $\frac{f}{1-f} = \frac{K_a}{[H^+]}$. Under all conditions considered, the inclusion of the Born energy lowers the fraction of charged acids in the polyelectrolyte layer. The effect is more pronounced as the polymer surface coverage increases. The shift in the titration curves due to the Born energy is largest for the pH value where the degree of charge is 1/2, which is defined as the apparent pK_a. For much lower and higher pH values than the apparent pK_a, the polyacid layer is either completely uncharged or charged, respectively and consequently the effect of Born energy diminishes. The apparent pK_a can be obtained experimentally, through titration, allowing comparison between experimental observations and theoretical predictions.[24,40,41] The apparent pK_a is shifted between 1 to 2 pH units, depending on the salt concentration and polymer surface density, compared to the pK_a of an isolated acid. For weak polyelectrolyte layers, the apparent pK_a not only shifts, but also the titration curves are wider than the bulk one and they are not symmetric. These effects have important implications: while the pK_a of an isolated acid determines the degree of charge for any pH value, the apparent pK_a of a polyacid layer does not contain this information. A polyacid layer behaves quantitively and qualitatively differently from an isolated acid molecule, as recognized even for bio polymers in the seminal work of Katchalsky and co-workers.[42–44] For further discussions on shifts in the apparent pK_a or equivalently salt concentration dependent titrations curves, see the works of Katchalsky and co-workers[42–44] and Refs. 1 and 45 and references therein. The inclusion of the Born energy in the description of a weak polyelectrolyte layer does not qualitatively change its behavior, but shifts the apparent pK_a by 0.2–0.3 units for the conditions considered in Figure 3, causing large changes in the average degree of charge of the polyacid layer and counterion distribution, as will be illustrated in Figures 5 and 6. It is important to recognize that the shift in the apparent pK_a is similar to the typical uncertainty of pK_a values reported in the literature and the shift expected due to the electronic inductive effects from the polymer backbone.[46] Therefore by slightly adjusting the intrinsic pK_a within the experimentally allowed range of values, we can obtain approximately the same result as in Figure 3(a) without explicitly including the Born energy into the free energy. This approach is, however, only an approximation since the shifts in the average degree of charge and apparent pK_a are dependent on the pH, salt concentration, and most prominently on polymer density as shown in Figure 3(b).

In order to explain the behavior of a weak polyelectrolyte layer and the influence of the Born energy, we first focus upon the case where the bulk pH is equal to the $pK_a = 5$. Figure 3 shows that the average degree of charge within the polyelectrolyte layer is lower than the isolated acid in bulk solution value of 1/2 for all salt concentrations and polymer surface coverages. The overall reduction of the degree of charge or deprotonation in the polymer layer with respect to the bulk is much larger than the effect of including the Born energy contribution. Taking into account the Born energy contribution can introduce large changes in the degree of charge of the polyacid layer (as we will show below), but it does not affect the overall qualitative behavior.

A charged group on a polyacid chain in a polyelectrolyte layer will experience much larger electrostatic repulsions than the same charged molecule in dilute solution due to the high polymer concentration. To compensate for the large energetic cost of these unfavorable electrostatic interactions, the system responds by the combination of three different mechanisms. First, the layer can recruit additional counterions to provide electrostatic screening. This process can occur only at the entropic cost of reducing the translational entropy of the counterions that are confined within the polymer layer. A second possibility involves stretching of the polyelectrolyte molecule in order to increase the average distance between charged acid groups. However, stretching of polyelectrolyte chain molecules results in a large loss of conformational entropy of the polyelectrolytes chains. Moreover, there is a limit on how much a polymer chain can stretch. Hence the possibility to reduce the unfavorable electrostatic interactions via chain stretching is limited. A third possibility is to shift the local acid-base equilibrium towards the protonated (uncharged) state thus changing the amount of charge. The cost associated with shifting the chemical equilibrium is proportional to the standard chemical Gibbs free energy $\Delta G_a^{\ominus}$ of the acid-base reaction. For weak polyelectrolytes, the free energy penalty associated with shifting the chemical equilibrium is less costly than that of counterion confinement. Therefore, the degree of charge is shifted towards the uncharged state within a weak polyelectrolyte layer as compared to the degree of deprotonation of the same acid molecule in solution. It should be stressed that notwithstanding the fact that the system has regulated its degree of charge down it still confines counterions and elongates its chains. However, due to the system's ability to regulate the amount of charge, ion confinement and chain stretching occur to a much smaller degree than for a non-regulating polyacid. The charge regulation mechanism allows a weak polyelectrolyte system, at least partially, to compensate for the unfavorable interactions within the layer and adopt a less unfavorable frustrated state.

For pH values much smaller than the apparent pK_a, the degree of charge is very low and the polyacid layer behaves essential as a neutral polymer layer, while for very high pH values all acid molecules are deprotonated. Consequently for both very low and very high pH values, the influence of the charge regulation, although still present, diminishes. Note that a single isolated carboxylic acid molecule in dilute solution would have a degree of charge of 99% at $pH = 7$ based on its intrinsic $pK_a = 5$; see the line labeled "bulk" in Figure 3. A polyacid layer made of the same acid groups has a much lower degree of charge and much higher pH values are required for the polyacid layer to have the same degree of charge.

Figures 3(a) and 3(b) present the degree of charge as function of pH from weak polyelectrolytes end-tethered to planar surfaces for different salt concentrations and polymer surface coverages. The figure shows that with decreasing salt concentration and increasing surface coverage the degree of charge of the acids groups decreases. Decreasing the salt concentration decreases the electrostatic screening and thus charges experience larger electrostatic interactions. The system can compensate these large energetic costs by counterion confinement and shifting the acid-base equilibrium towards

the uncharged state, i.e., changing the number of charges. As explained above, the later is less costly than counterion confinement and results in a decrease of the degree of dissociation. Increasing surface coverage increases the polymer density and, thus, the concentration of charged acid groups. This process leads to an increase of the electrostatic repulsion in the system, which can be compensated by down regulating the amount of charge, i.e., by shifting the acid-base equilibrium towards the uncharged state using the charge regulating mechanism as outlined above.

The effect of including the Born energy contribution influences the acid-base equilibrium in two distinct ways. First, the free energy cost associated with counterion confinement increases. Confining counterions in the polyelectrolyte layer not only results in a reduction of the translational entropy. But it also leads to an increase in the self-energy of the ions. Second, the Born energy adds an extra energetic penalty for introducing a proton-charged acid pair within the polymer layer. Effectively this penalty results in an increase of the free energy difference between its charged and uncharged state, i.e., the Gibbs free energy of the chemical equilibrium $\Delta G_a^{\ominus}$ increases. This increase is given by the $\Delta G_S(z)$ contribution presented in the chemical reaction equilibrium equation (18) that represents the difference in self-energy of forming a proton-deprotonated acid pair at position z and in the bulk aqueous environment. Adding the self-energy contribution leads to a further shift in the local acid-base equilibrium towards the protonated (uncharged) state of the acid groups as counterion confinement and deprotonation of the acid groups become energetically more unfavorable.

Figure 3(b) shows the effect of Born energy contribution as function of surface coverage. With increasing surface coverage the polymer density increases and consequently the concentration of (potentially) charged acids increases. Simultaneously with increasing polymer density the dielectric function decreases which results in an increase of the Born energy of the charged species. The combined effect is an increase in the energetic unfavorable electrostatic repulsions which the polyelectrolyte system tries to reduce by decreasing the amount of charges, i.e., shifting the local acid base equilibrium towards it uncharged state.

Here we like to point out that, for the highest surface coverages considered, the extra reduction in the degree of deprotonation arising from the inclusion of the Born energy contribution can be quite considerable. This result is illustrated in Figure 4 which shows the difference in degree of charge when no Born energy was considered and the case when the Born energy was included as function of pH for different surface coverages. For example, in the case of the high surface coverage of $\sigma_p = 0.40 \, \text{nm}^{-2}$, at $pH = 6$ and a salt concentration of $c_s = 100 \, \text{mM}$ the average degree of charge is $\langle f \rangle = 0.355$ when the Born energy is included and $\langle f \rangle = 0.435$ without inclusion of the Born energy. This result represents a difference in degree of charge of 0.08, a 18% change in the degree of charge. For the intermediate surface coverage of $\sigma_p = 0.20 \, \text{nm}^{-2}$ a difference of 0.04 is observed in the degree of charge due to the inclusion of the Born energy in the theory, while for the lowest surface coverage considered the change is only as 0.0067. These numbers indicate that the effect of
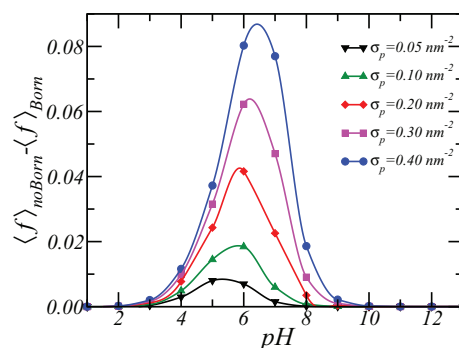

FIG. 4. The difference in degree of charge when no Born energy was considered and the case when the Born energy was included as function of pH for different surface coverages. The number of segments is $n = 50$. The salt concentration is $c_s = 100 \, \text{mM}$ and $pK_a = 5$.

Born energy can result in substantial changes in the degree of charge within a dense polyelectrolyte layer. For a pH value of 3 and lower, the total amount of charge is very low as the acid-base equilibrium is shifted almost entirely towards its protonated state. However, despite the fact that the total amount of charge is very low the inclusion of the Born energy still results in a reduction of the degree of charge, albeit that the absolute change in the average degree of charge is very small. The effect of Born energy on the degree of charge is largest for $pH \sim pK_{app}$. For pH values substantially above the pK_{app}, the effect of considering the Born energy reduces again. For a pH value above 9, the polyelectrolyte layer is almost completely charged ($\langle f \rangle = 0.995$ at $pH = 9$ for $\sigma_p = 0.40 \, \text{nm}^{-2}$) and inclusion of the Born energy, although still lowering the degree of charge, has negligible quantitative effect.

We next describe the local behavior within the layers. Figure 5 displays the local degree of charge as function of the distance from the surface for various salt concentrations and polymer surface coverages. Figure 5(a) corresponds to the case of a polyelectrolyte layer at a low polymer surface coverage of $\sigma_p = 0.05 \, \text{nm}^{-2}$, Figure 5(b) corresponds to the case of intermediate surface coverage of $\sigma_p = 0.20 \, \text{nm}^{-2}$, and Figure 5(c) correspond to the case of a high surface coverage of $\sigma_p = 0.40 \, \text{nm}^{-2}$, in all cases the bulk $pH = 5$. Close to the surface the polymer density is highest, hence the local degree of charge is the lowest. For the distal region of the polyelectrolyte layer, the polymer density drops and simultaneously the degree of charge increases and starts to approach the value of a single isolated acid monomer in dilute solution. Comparison between Figures 2 and 5 shows that the local degree of charge follows the polymer density. Obviously, the local degree of charge (Figure 5) shows the same trend as the global degree of charge (Figure 3), i.e., with decreasing salt concentration and increasing surface coverage the local degree of dissociation of the acids groups decreases. Figure 5(c) demonstrates that large changes can occur when the bulk salt concentrations is varied. It also shows that large differences in the local degree of charge can occur between the cases where the Born energy was included or not. Figure 5(c) shows that a reduction of up to approximately 20% (for a bulk salt concentration of $c_s = 200 \, \text{mM}$) can occur in the (local) degree of charge. This result indicates that the effect
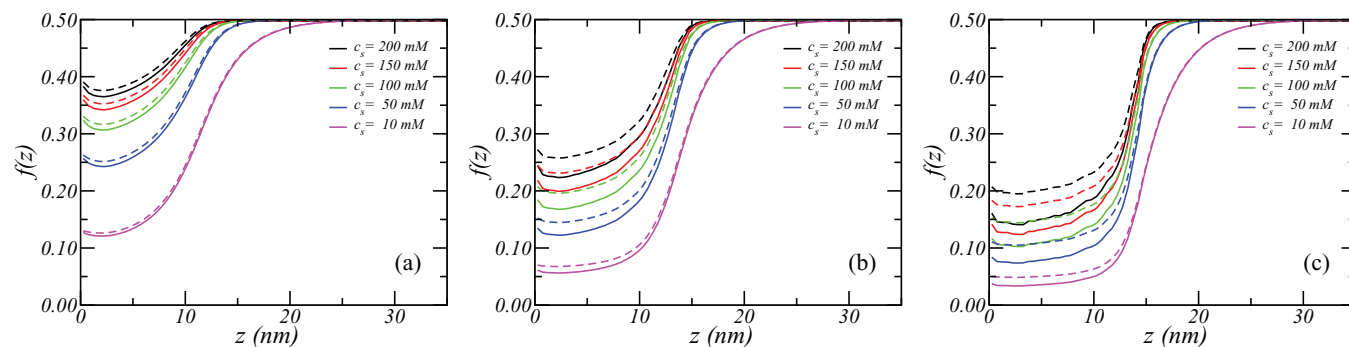
FIG. 5. The fraction of charged monomers as function of the distance from the planar surface for different salt concentrations for a surface coverage of (a) $\sigma_p = 0.05\,\mathrm{nm}^{-2}$, (b) $\sigma_p = 0.20\,\mathrm{nm}^{-2}$, and (c) $\sigma_p = 0.40\,\mathrm{nm}^{-2}$. $pH = pK_a = 5$. The solid lines correspond to the case where the Born energy contribution is included in the free energy. The dashed lines correspond to the case where the Born energy contribution was not included.

of Born energy can result in substantial changes in the degree of charge within a dense polyelectrolyte layer.

To further illustrate this point, we present in Figure 6 the distribution of the charged species. The pH value is equal to 5 and the bulk salt concentration is 10 mM for the same surface coverages as Figure 5. The figures show the charge density distribution as a function of distance from the surface for the positive (sodium) ions, the negative (chloride) ions, the charged monomers, and the total charge density. The charge distributions of the protons and the hydroxyl ions are not shown since on the scale of the figure their concentration is too small to be visible. First, we notice that for all cases the concentration of (positively charged) counterions is much larger inside the polyelectrolyte layer than in the bulk aqueous solution, because the counterions are confined within the polymer layer in order to provide electrostatic screening. Second, with increasing polymer density the amount of counterions increases because the concentration of polyacids increases. It is important to emphasize that while the fraction of deprotonated acid groups decreases with increasing surface coverage, the total charge on the polyacid layer increases. The counterions almost complete compensate for the negative charges of the polyacids, as the total charge density within the layer is much smaller than the charge density of the polyacids. Finally, the effect of the Born energy is more pronounced with increasing polymer density. As explained before the de-

gree of charge decreases when the Born energy is included in the free energy. Moreover, the difference grows with increasing polymer density. Therefore, the distribution of counterions, which is closely coupled to the distribution of charged polyacid monomers, will also decrease. The effect of Born energy can be quite large: the concentration of counterions reduces by approximately 25% for the intermediate surface coverage and by approximately 50% for the high surface coverage when the Born energy contribution is included. It is interesting to note that while the polymer charge and the counterion distribution changes significantly with the explicit consideration of the Born energy the total charge distribution is basically identical. On the scale of the graph the difference in the total charge density are not visible.

Figure 7 shows the electrostatic potential as function of distance from the surface for various salt concentration. The remaining conditions (pH and surface coverage) correspond to those of Figure 6(c). Interestingly, the effect of the Born energy contribution on the electrostatic potential is much smaller than its effect on the charge distribution of the counterions and the polyacids. The changes in the electrostatic potential are relatively small. In principle, one would expect changes in the electrostatic potential because the Born energy introduces large changes in the concentration of charged groups within the film. However, the effect is small because the electrostatic potential is determined by the total charge
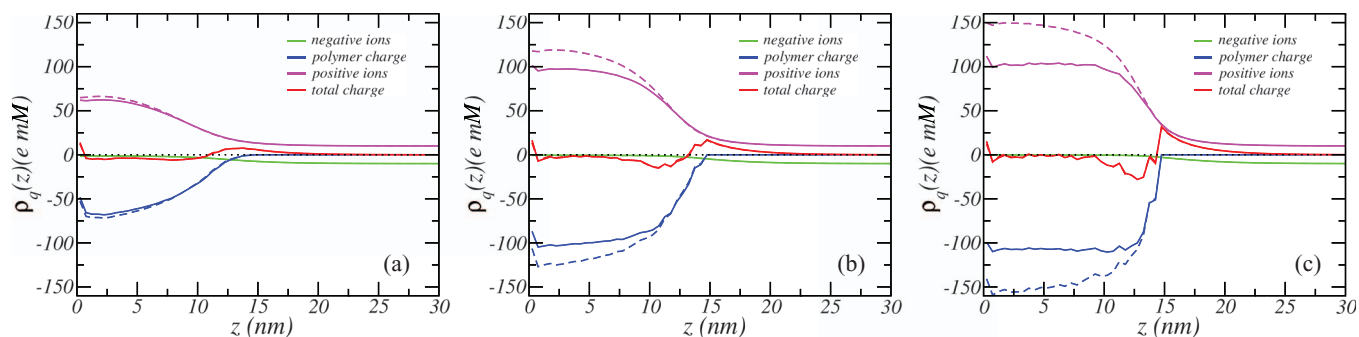

FIG. 6. The distribution of charges as function of the distance from the planar surface for (a) $\sigma_p = 0.05\,\mathrm{nm}^{-2}$, (b) $\sigma_p = 0.20\,\mathrm{nm}^{-2}$, and (c) $\sigma_p = 0.40\,\mathrm{nm}^{-2}$. The polymer chain length is $n = 50$ with $pK_a = 5.0$. The bulk solution is characterized by $pH = 5.0$ and a salt concentration of $c_s = 10\,\mathrm{mM}$. The solid lines correspond to the case where the Born energy contribution is included in the free energy. The dashed lines correspond to the case where the Born energy contribution was not included. Note that on the scale of the figure the total charge distribution and the charge distribution of the negative ions with and without Born energy are indistinguishable.
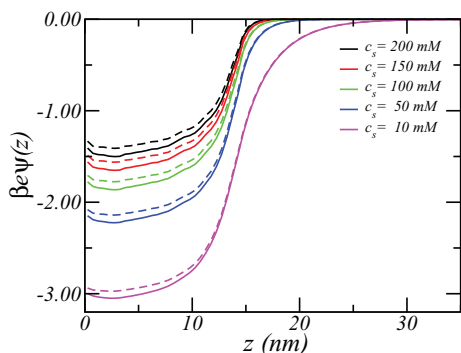
FIG. 7. The electrostatic potential as function of the distance from the planar surface for $\sigma_p = 0.4\,\text{nm}^{-2}$. The bulk solution is characterized by $pH = 5$ and $pK_a = 5$. The solid lines correspond to the case where the Born energy contribution is included in the free energy. The dashed lines correspond to the case where the Born energy contribution was not included.

density distribution and not by the partitioning of the charged species. The total charge density does not significantly change and consequently the electrostatic potential difference is only due to the small differences in the total charge, barely seen in Figure 6. The total charge density was not significantly influenced by the Born energy because the system tends to achieve local charge neutrality in order to optimize the electrostatic contribution to the free energy. Local net charges can only be maintained at high energetic penalties. The system avoids the energetic unfavorable interactions by changing the local amount of charge by shifting the local acid-base chemical equilibrium and changing the local concentration of mobile ions (i.e., counterion confinement). Hence the total charge density does not change and as a result the electrostatic potential was not significantly altered. However, the partition of the different ionic species changes because the charge regulation is coupled to the Born energy and the polymer conformations. The same argument explains why we do not observe significant changes in the density profile of the polyelectrolyte layer.

B. Importance of the Born energy contribution in experimental observables

1. Thermodynamic properties of weak polyelectrolyte layers

Next, we consider the influence of the Born energy on thermodynamic quantities by studying the interaction between two parallel planar surfaces where one of the surfaces is modified by end-tethered weak polyelectrolyte chains. The interaction between a polymer coated surface and a second external surface can be measured by, for example, the surface force apparatus[28,47] or atomic force microscopy.[48] It is therefore important to address the importance of the Born energy on the interactions between a polyelectrolyte-coated surface and a flat uncoated surface.

Figures 8 display the change in free energy per unit area as a function of the distance between the two planar surfaces. As the separation decreases, the free energy increases due to the combination of steric and electrostatic repulsions. The steric repulsions are primarily due to loss of polymer configurational entropy and osmotic pressure, while the electrostatic
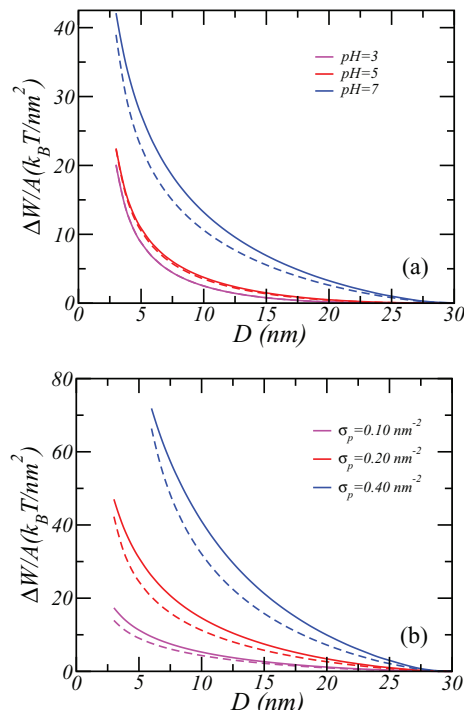

FIG. 8. Effective interaction between two surfaces: free energy per unit area versus distance between two planar surfaces, where one of the surfaces is modified with end-tethered weak polyelectrolytes for (a) different pH values for a surface coverage of $\sigma_p = 0.20\,\text{nm}^{-2}$ and salt concentration of $c_s = 50\,\text{mM}$ and (b) for different surface coverages at $pH = 7$ and $c_s = 100\,\text{mM}$. The length of the polymer equals $n = 50$ and $pK_a = 5.0$. The solid lines correspond to the case where the Born energy contribution is included in the free energy. The dashed lines correspond to the case where the Born energy contribution was not included.

repulsions arise mostly from counterion confinement.[15,49] Figure 8(a) shows the interaction free energy for fixed surface coverage at different pH values, while Figure 8(b) shows the effect of surface coverage at a given pH on the interactions. With increasing pH and surface coverage, the repulsions increase as both the steric repulsions and the electrostatic interactions increase. Focusing on Figure 8(a), we predict that with increasing pH, the free energy is larger and the effect of including the Born energy on the interaction free energy also increases. For pH 3, the degree of charge is very low with or without Born energy. Hence the repulsions are almost solely arising from the steric repulsions. Consequently the difference in free energy with and without Born energy is very small. For pH 5, we observe a small difference and for pH 7, we observe a substantial difference in the free energy when comparing the case of the free energy with and without Born energy. With increasing pH, the polyacid groups acquire charge, as explained previously, and the electrostatic repulsions due to counterion confinement increase. Similarly, with increasing surface coverage the total charge in the layer increases and the total free energy increases. However, the total degree of charge is lower when the Born energy contribution is considered. Despite the fact that including the Born energy reduces the degree of charge and the density of the counterions, the interaction free energy is higher when the Born energy is included than when it is neglected. When the system is confined the mobile ions will not only loss translational entropy but

are energetically penalized by an increase of the Born energy, therefore the repulsions increase when the Born energy is included. When the two surfaces get closer together the degree of charge of the polyelectrolytes decreases as the acid-base equilibrium shift towards the uncharged state under influence of the increased polymer concentration. It is important to note the difference in shape of the free energy curve as the Born energy is included. For sort distances the free energy difference between Born energy and no Born is smaller than at larger distances. Therefore, the relative importance of the Born energy contribution decreases. At short distances the steric repulsions dominate, while at larger distances the electrostatic repulsions in the form of counterion confinement coupled to the acid-base equilibrium are the most important contribution to the interaction free energy. Observe that in all cases the repulsions diverge at short separations. This is due to the finite availability of volume and the excluded volume interactions of the polymer chains. Finally, while the strength of the repulsions increase when the Born energy contribution is taken into account, its qualitative behavior is not changed.

2. Capacitance of polyelectrolyte-modified electrodes and conductivity of polyelectrolyte-modified nanopores

The inclusion of the Born energy contribution in the molecular theory comes at the cost of increased complexity. It is therefore important to determine which theoretical predictions require this contribution and which ones can be determined with the more approximate theory. We have shown that the main effect of the Born energy contribution on the molecular organization of an end-grafted polyacid layer is to decrease the concentration of mobile ions by uncharging the weak acid groups (i.e., via a charge-regulation mechanism). We therefore focus our attention here on its effect on two experimental observables that are known to depend strongly on the concentration and distribution of mobile ions: the capacitance of polyelectrolyte-modified electrodes and the conductivity of polyelectrolyte-modified nanopores.

The differential capacitance of a metal electrode is given by the derivative of its surface charge with respect to the applied potential:

$$C = \frac{\partial \sigma_M}{\partial V}. \qquad (20)$$

The capacitance of an electrode is very relevant in electro-analytical and energy storage applications, for example, materials with a high capacitance per unit volume (such as carbon nanomaterials of high specific area) are used as supercapacitors. The capacitance depends on the dielectric environment close to the interface, the salt concentration, and the presence and conformation of adsorbates. Previous theories to predict the capacitance of an electrode were the Gouy-Chapmann and Stern models for bare electrodes[50] and the Smith and White model for surfaces modified with weak acids.[51,52] Recently, a molecular theory was reported to model polyelectrolyte-modified electrodes that explicitly considers the presence of absorbed macromolecules and their conformational degrees of freedom, the acid-base and redox equilibria, and the electrostatic and non-electrostatic interactions in the system, although it neglected the Born Energy contribution[53,54] the predictions of the theory were in very good agreement with experimental observations. In Figure 9, we study the effect of the Born energy contribution on the
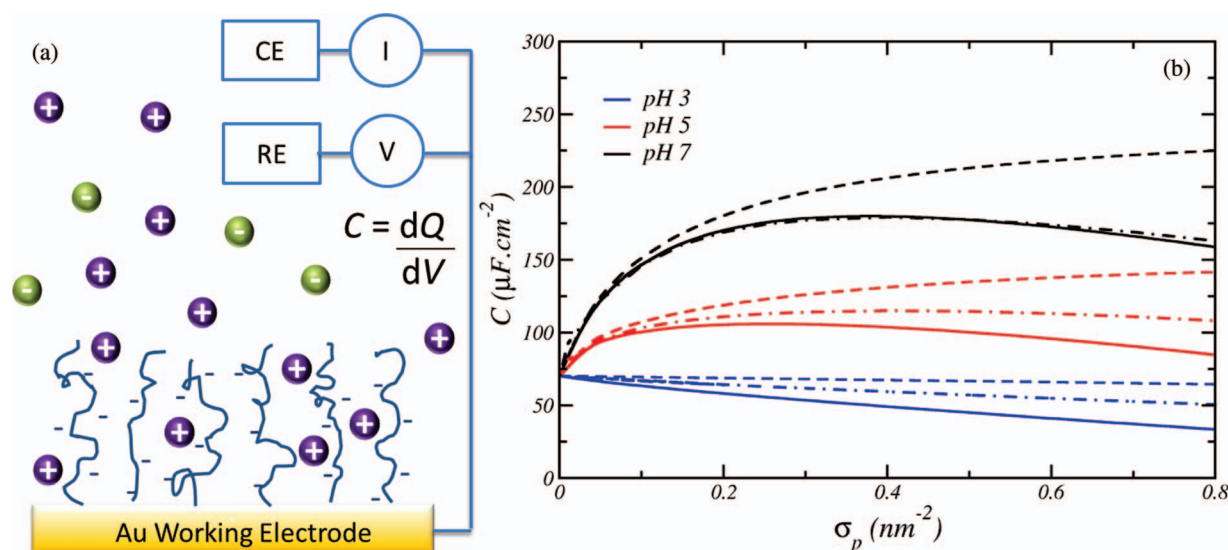

FIG. 9. (a) Schematic of the polyelectrolyte-modified electrode: A gold electrode is modified with an end-grafted polyacid brush and immersed in an electrochemical cell containing a counter (CE) and a reference (RE) electrode. In the absence of redox reactions, the system behaves as a capacitor: as a potential difference is applied between the Au working electrode and the reference electrode, the surface of the Au electrode is charged. The capacitance of the system is defined as the derivative of the charge in the working electrode with respect to the applied potential. (b) Comparison between the capacitance of the system shown in A as a function of the polyelectrolyte surface coverage and for three different solution pHs. Different styles of lines correspond to calculations using different approximations in the formulation of the molecular theory. The solid lines are predictions including the Born self-energy. The dash-dotted lines are predictions neglecting the Born energy, but assuming a position-dependent dielectric function. Finally, the dashed lines are predictions neglecting the Born energy and assuming an homogeneous dielectric function of 78.54 (i.e., pure solvent). Calculation conditions: $pK_a = 5.0$, bulk salt concentration $c_{salt} = 0.1$ M, and chain length $n = 50$. The potential of the working electrode was set to the potential of zero charge of a bare metal electrode.
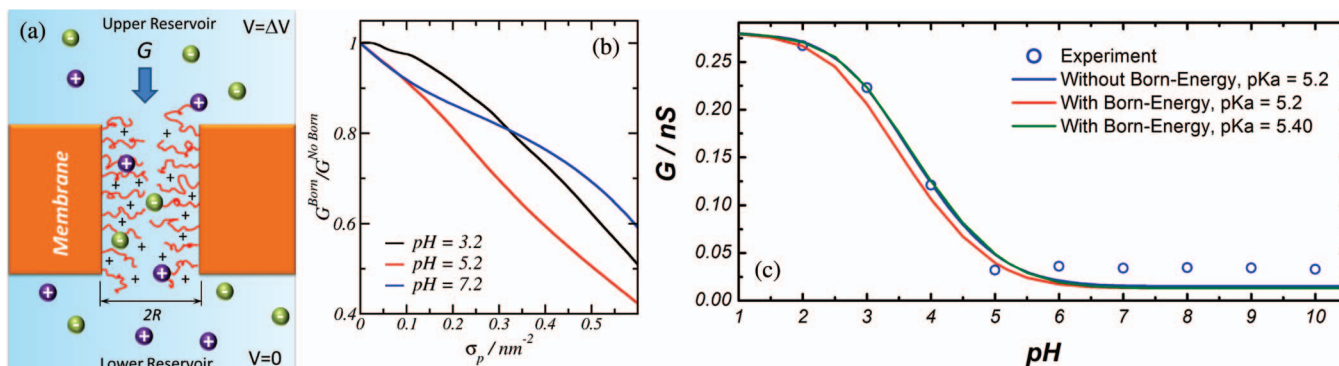
FIG. 10. (a) Schematic representation of a polyelectrolyte-brush-modified nanochannel: the cylindrical nanochannel of radius R and length L ($L \gg R$) is modified with an end tethered layer of poly(4-vinyl pyridine), 4PVP. Each segment in 4PVP can be either positively charged (protonated) or neutral, depending on the apparent pK_a and the pH. The channel is connected to two macroscopic reservoirs containing aqueous 0.1 MKCl solutions. The mobile ions in the system (K^+, H^+, OH^- and Cl^-) flow through the pore upon applying an electric potential difference between reversible electrodes located at the reservoirs (see Refs. 23 and 55). (b) Ratio of the conductivity of the nanochannel determined from the molecular theory including the Born energy contribution (G^{Born}) to that determined in the absence of this contribution (G^{NoBorn}) as a function of the polyelectrolyte grafting density (σ_p) for different pHs ($pK_a = 5.2$). The conductivities have been determined from the concentration of ions within the pore predicted by the molecular theory using the Goldman Constant Field approximation, Eq. (21). (c) Comparison of experimental conductivity data[56] (open circles) and the predictions of the molecular theory with and without the Born contribution for different values of pK_a. Calculation conditions: bulk salt concentration = 0.1 M, chain length = 28, $R = 7.5$ nm, and $L = 12 \mu m$.

differential capacitance of a polyelectrolyte-brush modified electrode as a function of the polyelectrolyte brush grafting density and pH (the polyelectrolyte model is the same as that discussed in Sec. III A). In addition to the theory reported in this work which explicitly incorporates the Born energy contribution (shown in solid lines), we also considered a theory without this contribution (dashed-dotted lines), as well as a theory without the Born energy contribution and assuming that the dielectric function is equal to that of the pure solvent ($\epsilon_w = 78.54$) everywhere. It should be mentioned that in order to properly treat the metal electrodes, the boundary condition of the Poisson equation in Eq. (17), changes from constant surface charge density to constant surface potential. The first interesting result from Figure 9 is that the case of no varying dielectric function produces a capacitance that monotonically increases with the surface coverage of the polymer, while considering the correct local dielectric constant produces a maximum in the capacitance-surface coverage plots. This non-monotonic behavior arises from the opposing effects of increasing the polyelectrolyte grafting density on the system capacitance. On the one hand, increasing σ_p boosts the concentration of ionizable groups and ions, which screens the charge of the metal electrode and therefore increases the capacitance of the system. On the other hand, increasing the polyelectrolyte grafting density decreases the value of the dielectric function within the layer, which destabilizes the charge on the electrode and therefore decreases the capacitance.

Comparison between the capacitances calculated with and without the Born contribution in Figure 9(b) shows that the theory with Born energy always predicts a smaller capacitance than the theory without Born energy, because the Born energy contribution decreases the concentration of ions and charged groups in the layer. As explained in Sec. III A, the Born energy contribution is important only for large polyelectrolyte volume fractions, i.e., large surface coverage. Interestingly, including the Born energy term in the free energy affects the capacitance for pH 3 and pH 5, but not for pH

7, since at this pH most of the acid groups are deprotonated ($pH > pK_a = 5$) and thus charge regulation is of minor importance. It is worthwhile to mention that in many practical applications (such as the polyelectrolyte-modified electrodes studied in Refs. 53 and 54), a low-dielectric thiol layer is intercalated between the polyelectrolyte layer and the metal electrode. Since the capacitance of this layer dominates the total capacitance of the system, the contribution of the polyelectrolyte layer to the total capacitance (and thus the effect of the Born energy contribution) is expected to be much smaller than that discussed here.

In our second example, we consider a long nanochannel modified by poly(4-vinyl pyridine) (4PVP) end-grafted chains (see Figure 10). Poly(4-vinyl pyridine) is a polybase (as opposed to the polyacid studied in previous examples) and, therefore, each pyridine unit can be either electrically neutral or bear a single positive charge, depending on its apparent pK_a (e.g., the monomer will be positively charged for $pH \ll pK_{app}$). The nanochannel connects two reservoirs, each one containing a 0.1 M solution of a 1:1 electrolyte and a reversible electrode. When a potential difference ΔV is applied to the electrodes, ions flow through the channel producing a current I; the conductivity of the channel is $G = I/\Delta V$. In previous work,[23,55] we have shown that the ion conductivity of polyelectrolyte-modified nanopores is determined by the concentration of ions within the pore. For very long channels, G can be determined with the Goldman Constant Field approximation as[57]

$$G = \frac{I}{V} = \frac{2\pi}{L}\frac{F^2}{RT}\sum_{i=\{K^+,Cl^-,OH^-,H^+\}} q_i^2 D_i \int_0^R c_i(r)r\,dr,$$
(21)

where L is the length of the pore, F is the Faraday constant, q_i and D_i are the charge and diffusion coefficient of the ion i, respectively, and $c_i(r)$ is the concentration of the ion i at r in equilibrium conditions, which is determined from the molecular theory. Of course, the theory is applied to the proper cylindrical geometry as required by the problem.[15,23]

Application of the Goldman Constant Field approximation implies that we do not consider hydrodynamic interactions and electophoretic flow. For long nanochannels, it has been shown that the electro-osmotic contribution to the conductivity is negligible.[58] In Figure 10, we show the ratio of the conductivity calculated with the molecular theory including Born energy (G^{Born}) to that calculated neglecting it (G^{NoBorn}) as a function of the polyelectrolyte surface coverage and pH. As expected, the effect of the Born Energy contribution on the conductivity is larger for high grafting densities and pHs close to the pK_a.

In previous work, we have compared the predictions of the molecular theory (without Born energy contribution) to the pH-dependent experimental conductivity reported by Yameen et al.[56] We find here that in the conditions of the experiments ($\sigma_p = 0.2 \, nm^{-2}$), neglecting the Born energy contribution introduces an error of approximately 10% in the conductivity (Figure 9). We note that using $pK_a = 5.2$, the calculation including the Born energy contribution shows a worse agreement with the experimental data than the theory without Born energy. However, a very good agreement between experiment and the theory with the Born energy contribution can be obtained by shifting the bulk pK_a of the pyridine unit from 5.2 to 5.4. The difference in pK_a of 0.2 is smaller than the uncertainty arising from electronic inductive effects: due to the presence of a methylene group in the para position to the pyridinic N, the pK_a is expected to be anywhere between that of pyridine (5.23)[46] and that of 4-ethyl pyridine (5.89).[46] In summary, in the conditions of the experiment, the effect of the Born energy contribution can be offset by shifting the pK_a by a small value and it is thus of minor importance.

IV. CONCLUDING REMARKS

In this work, we presented the inclusion of the Born energy into a general molecular theory describing the properties of weakly chargeable end-tethered polyelectrolytes. The molecular theory explicitly includes the conformations of the polymer chains, excluded volume, van der Waals, and electrostatic interactions as well as acid-base chemical equilibrium. To account for the very different dielectric environments that the polymers and the water solution provide, we have included a varying dielectric function in the theoretical description. A varying dielectric function also requires the inclusion of the self- or Born energy for the electrostatic charges[25, 26] which we incorporated in the theory. Results for the average and position-dependent charge of acid groups in end-tethered polyelectrolyte layers, as well as polyelectrolyte and counterion density distributions were presented for various conditions. We found that inclusion of the Born energy does not significantly influence the electrostatic potential and the density distribution of the polymer for the conditions investigated. However, a clear effect on the degree of charge and on the counterion distribution within the layer is predicted. For all conditions considered, the degree of charge predicted by the molecular theory with Born energy is lower than that predicted by the molecular theory that did not take into account the Born self-energy. Inclusion of the Born energy contribution in the theoretical description of a weak polyelectrolyte layer leads to an increase in energetically unfavorable electrostatic interactions. The system can mitigate the extra unfavorable interactions by shifting the acid-base equilibrium towards its uncharged state.

For low surface coverages, the effect of including the Born energy is small. However, the effect on the degree of charge grows with increasing surface coverage of the end-tethered polyelectrolytes and is largest for pH values comparable to the apparent pK_a. The inclusion of Born energy can significantly reduce the amount of counterions and the degree of charge of end-tethered weak polyelectrolyte layers as compared to predictions not including the self-energy. We investigated the effect of the Born energy upon the capacitance of a polyelectrolyte coated electrodes and the conductance of polyelectrolyte-brush-modified nanochannels as both of these experimentally observable quantities are strongly dependent on the concentration of counterions. We found that the capacitance of the polymer-modified electrode is lower when considering the Born energy than when neglecting it. Similarly the conductance of the nanochannel decreases when including the Born energy into the calculation. Good agreement with experimental observations could be obtained for the conductance provided the intrinsic pK_a was chosen appropriately. Namely, we found that a small change in the pK_a, within the range of the experimental uncertainty in its determination, leads to very good agreement with experimental observations.

The inclusion of the Born energy causes an increase in the strength of the repulsions between a weak polyelectrolyte coated planar surface and a second confining surface. The effect becomes substantial for large pHs and high polymer density. These results indicate that taking into consideration the repulsion arising from the Born self-energy can be important for brushes made of strong polyelectrolytes and for dense and highly charged polyelectrolyte layers.

There is a large amount of theoretical work devoted to understanding the behavior of weak tethered polyelectrolyte layers which has provided us with a good general understanding of these systems.[1, 5, 6, 8, 10, 11, 59–61] These works, as well as previous work based on the molecular theory, did not consider the Born energy contribution. Good agreement has been found between theoretical predictions that neglected the Born energy contribution and experimental observations, such as the height of a layer of polyacrylic-acid end-tethered to planar surface,[21, 22] the conductivity of nanochannels modified by weak polyelectrolytes,[23] and the amount of charge of acidic ligand-coated nanoparticles.[24] So first the question that arises is why was inclusion of the Born energy not necessary to achieve good agreement with experiments and second under which conditions do we need to consider the Born energy contribution in order to understand the properties of weak polyelectrolyte layers. The answer to the first part is threefold. First, for low surface coverages of the polymer layer the effect of including the Born energy contribution is small. Second, as demonstrated here, the inclusion of the Born energy does not qualitatively change the behavior of a weak polyelectrolyte layer. Third, as shown in Figures 10(a) and 3, changes in the apparent pK_a (which influences the properties such as the conductance) as brought about by considering explicitly the Born energy are of a similar order of magnitude as the typical

uncertainties in the intrinsic (bulk) pK_a. Hence, shifting the bulk pK_a within the experimental established range of values usually will suffice to obtain a good agreement with the experimental properties of weak polyelectrolyte layers. Note that this reasoning does not seem to be applicable to thermodynamic properties, such as the free energy. The most important conclusion is that the most significant effect is to take into account explicitly the ability of the layer to regulate its charge through acid-base equilibrium. The effect of the Born energy becomes a second order effect since most of the properties of the layer are determined by the total charge, which changes in a very small amount whether the Born energy is considered or not. However, the distribution of ions is variable since the degree of charge as well as the presence of counterions is significantly reduced when properly considering the Born energy in high polymer density environments. In the range of experimentally relevant systems the polymer density is not enough to have a major effect and therefore a small shift in the bulk pK_a is enough to properly describe the system.

We would like to point out that while the molecular theory describing tethered weak polyelectrolytes explicitly includes the coupling between molecular interactions, conformational properties, and chemical equilibrium, it is still an approximate (mean-field) theory. Therefore, there are a number of aspects of the theory that might require improvement such as the possibility of ion-ion pairing between the mobile ions and counterion condensation onto charged polyacid monomers. These effects are expected to be particularly important for polyelectrolyte layers that have a high charge density, the same condition where the Born energy effect on structural and thermodynamic properties is most prominent. Moreover, the effect of the Born energy can become important for multivalent ions, as their self-energy is much larger than that of the monovalent mobile ions considered here, but for multivalent ions, ion-condensation will also be a very important charge regulation mechanism. Ion-ion pairing and ion condensation can be included into the molecular theory by considering them as chemical reactions[62] (see, for example, the work by Barbosa *et al.*[63] or Cheng *et al.*[64]). Finally, it is not clear what is the appropriate form of the constitutive equation for the dielectric function. While previous work has shown that different functional forms lead to essential identical behavior in polyelectrolyte layers,[15] one needs to question the use of macroscopically derived response functions in microscopic theories. However, that is beyond the scope of this work and in most practical applications, the use of these constitutive equations provides a reasonable description of the systems of interest.

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