I. INTRODUCTION

Numerous papers have been written on various aspects of the electric double layer a solid-water interface.\textsuperscript{1-5} However, not enough attention has yet been paid on physics and chemistry of ionizable solid surfaces in contact with an aqueous electrolyte solution. As a well-known example,\textsuperscript{6,7} Behrens et al.\textsuperscript{15–23} first presented a model of surface ionization using the mass action law as the boundary condition of the Poisson-Boltzmann (PB) equation, where $\Gamma_0$ and the dissociation constant $K_\alpha$ are relevant parameters. They determined $\alpha$, the charge distribution, and the electric potential self-consistently. Behrens et al.\textsuperscript{15–18} solved these equations accounting for a potential drop across the Stern layer formed on a solid surface in water. These theories are based on one-dimensional (1D) calculations of the PB solutions for symmetric ionizable surfaces. Behrens et al. also devised a formula for the ionization of large colloidal particles.

In this paper, we construct a free energy functional for the ion densities $n_i$ and $\alpha$ in applied field, accounting for the chemical reactions in the bulk and on the surface. We then examine the effect of sodium hydroxide NaOH at a low density $n_0$, where the hydroxyl density $n_{\text{OH}}$ and the proton density $n_{\text{H}}$ are related by the dissociation law $n_{\text{OH}}n_{\text{H}} = 10^{-14} \text{mol}^2/L^2$ in bulk water.\textsuperscript{24} Thus, adding NaOH serves to decrease $n_{\text{H}}(0)$ and increase $\alpha$. In experiments, the surface ionization due to deprotonation increased with addition of OH$^-$ (with increasing pH).\textsuperscript{15,25–28} We also apply an electric field to the system attaching a planar electrode with a surface charge density $\sigma_m$. Then, there arises another kind of charge regulation. We assume that the electric double layer next to the film is determined by the effective density $\sigma_{\text{eff}} = -e\Gamma_0\alpha + \sigma_m$. Thus, if $\sigma_m$ is positive (negative), the cations including the protons tend to be repelled from (attracted to) the film, leading to an increase (a decrease) in $\alpha$. We have $\alpha \to 0$ for $\sigma_m < 0$ and $\alpha \to 1$ for $\sigma_m > e\Gamma_0$. However, in the range $0 < \sigma_m < e\Gamma_0$, marked self-regulation behavior emerges, where $\alpha$ approaches $\sigma_m/e\Gamma_0$ and $\sigma_{\text{eff}}$ nearly vanishes. In this effect, the NaOH density $n_0$ needs to be smaller than a characteristic density $n_c$, where $n_c$ is much larger than the hydroxyl density $10^{-7}$ mol/L in pure water. For small wall separation $H$ and for not small $\sigma_m$, screening of the surface charges can only be partial, leading to a negative disjoining pressure $\Pi_d$ with large amplitude. For sufficiently large $n_0$ with small $H$, screening can also be achieved leading to a large positive $\Pi_d$.

Furthermore, in a mixture solvent, the dissociation on solid surfaces can strongly depend on the local solvent composition $\phi$ as well as the solvation of ions in aqueous mixtures.\textsuperscript{30,31} In our previous paper,\textsuperscript{32} small variations of $\phi$ around the colloid surfaces induced significant changes in $\alpha$ and the ion distribution. Thus, there can be a strong coupling between $\phi$ and the ionization in mixture solvents, which alters adsorption and wetting on the surfaces and the interaction among the colloidal particles.
In polyelectrolytes and charged gels, the dissociation on polymer chains is governed by local environments and is highly fluctuating in space and time. This can strongly affect colloid-globe transition and phase separation, particularly when a second fluid component (cosolvent) is added to a water-like solvent. A first order phase transition of weak-to-strong ionization was also predicted on ionizable rods in a mixture solvent. In phase separation, α can be very different in the two phases. With addition of alcohol to water, precipitation of DNA has also been observed, where ionization of DNA is favored in water-rich environments.

The organization of this paper is as follows. In Sec. II, we will present a coarse-grained Ginzburg-Landau free energy functional, which includes the electrostatic contributions from the Stern layers and the dielectric film. In Sec. III, we will present numerical results for silica-water interfaces for thick cells. In Sec. IV, we will discuss the ionization on carboxyl-bearing surfaces. In Sec. V, we will present results for thin cells.

II. THEORETICAL BACKGROUND

We illustrate our system in Fig. 1, where a cell contains liquid water and ions in ambient conditions (T = 300 K and ρ = 1 atm) in the region 0 < z < H and a dielectric film is in the region −ℓ < z < 0. For example, we suppose a ultra-thin silica oxide film with silanol groups in water. To apply electric field to the system, we place metallic walls at the two ends in the regions z < −ℓ and z > H. In our theory, we can fix the applied potential difference V or the electrode surface-change density σm.

The cell lengths in the lateral directions are much longer than H such that the edge effect is negligible. All the physical quantities are coarse-grained smooth variables depending only on z. Hereafter, the Boltzmann constant will be set equal to 1.

FIG. 1. Illustration of geometry. Two parallel metallic plates are placed at bottom (z < −ℓ) and top (z > H) with charge densities σm and a potential difference V. A dielectric film with thickness ℓ is on the bottom metallic plate (−ℓ < z < 0). At z = 0, ionizable groups A+ and H+ with a fraction α. Water molecules are under strong influence of the walls in Stern layers (0 < z < dH and H−dH < z < H). Protons also come from dissociation of water. MOH dissociates into M+ and OH−. If a battery is connected, V can be controlled, while the metal surface charge density σm fluctuates. If it is disconnected, σm becomes fixed. Furthermore, if a small capacitor is connected, σm can be changed by a small fixed amount (see Appendix A).

A. Chemical reactions in bulk and on surface

In the cell, we initially add a base MOH at a low density. It dissociates into mobile univalent cations M+ and hydroxide anions OH− as

\[
\text{MOH} \rightleftharpoons \text{M}^+ + \text{OH}^-. \tag{1}
\]

In addition, a very small fraction of water molecules dissociate into H+ and OH− as

\[
\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \tag{2}
\]

We use the notation H+, though the protons exist as hydronium ions H3O+ with a trigonal pyramidal structure in liquid water. In this paper, we neglect the internal structures of these ions. The local number densities of MOH, M+, OH−, and H+ are written as nMOH(z), nM+(z), nOH−(z), and nH+(z), respectively, which are coarse-grained smooth functions of z in our theory. The charge density ρ(z) is written as

\[
\rho = e(n_\text{M}^+ + n_\text{M}^- - n_\text{OH}^-). \tag{3}
\]

In chemical equilibrium, the mass action laws hold

\[
n_\text{MOH}/n_\text{MOH} = K_b, \tag{4}
\]

\[
n_\text{OH}^-/n_\text{MOH} = K_a, \tag{5}
\]

where \(K_b\) and \(K_a\) are the dissociation constants. For NaOH, we have \(K_b = 10^{-14}\) mol/L = 0.06 nm−3. However, \(K_a^{1/2}\) is much smaller (=10−7 mol/L = 6 x 10−8/ nm2).

In a thick cell, a homogeneous bulk region appears far from the walls, where ni assume bulk values, written as \(n_i^0\). They satisfy Eqs. (4) and (5) and the charge neutrality condition \(n_M^0 + n_H^0 = n_{OH}^0\). We introduce the bulk density of M atoms by

\[
n_0 = n_{M}^0 + n_{OH}^0. \tag{6}
\]

See Fig. 2(a) for \(n_0^0\) vs \(n_0\) for M=Na. For such a strong base with large \(K_b\), we can well assume \(n_0 \ll K_b\) to find

\[
n_M^0 \equiv n_0, \quad n_{MOH}^0 \equiv n_{OH}^0 n_0/K_b \ll n_0, \tag{7}
\]

where \(n_{MOH}^0 \ll K_b\). From \(n_0 = (1 + n_{OH}^0/K_b)(n_{OH}^0 - n_{H}^0)\), we can express \(n_0\) in terms of \(n_{OH}^0\) as

\[
n_0 \equiv n_{OH}^0 = n_{H}^0 + n_{OH}^0 - K_b n_{OH}^0. \tag{8}
\]

In pure water, we have \(n_0 = 0\) and \(n_{OH}^0 = n_{H}^0 = K_w^{1/2}\). For \(n_0 \gg K_w^{1/2}\), we obtain \(n_{OH}^0 \equiv n_0\) and \(n_{H}^0 \equiv K_w/n_0 \ll K_w^{1/2}\). In

FIG. 2. Chemical reactions in this paper. (a) Equilibrium bulk densities \(n_i^0\) (i = NaOH, Na+, OH−, and H+) divided by \(K_w^{1/2}\) vs \(n_0/K_w^{1/2}\), where \(n_0\) is the bulk density of Na atoms. (b) Equilibrium α vs \(n_0/K_w\) from Eq. (11).
the following figures, supposing a strong base, we will use \( n_0 \) to represent the amount of the added base. However, our theoretical results will be expressed in terms of \( n_{OH}^0 \) and \( n_{H}^0 \) and will be valid for arbitrary \( K_b \). In our figures Eq. (8) holds, so they can be used even for weak bases\(^2^8\) if \( n_0 \) is related to \( n_{OH}^0 \) by Eq. (8).

On the surface of the dielectric film at \( z = 0 \), ionizable groups AH are distributed with a surface density \( \Gamma_0 \). No dissociation is assumed on the upper metal surface. Depending on the local pH near the surface, a fraction \( \alpha (0 < \alpha < 1) \) of these groups dissociate as\(^1^6\)

\[
AH \rightleftharpoons A^- + H^+.
\]

(9)

Here, \( A^- \) anions remain on the surface \( z = 0 \), while the dissociated protons are mobile in water. The surface charge density due to \( A^- \) at \( z = 0 \) is

\[
\sigma_A = -e\Gamma_0\alpha.
\]

(10)

Let \( n_{H}(0) \) be the proton density immediately close to the dielectric film in water. Then, the surface mass action law in chemical equilibrium is expressed as\(^1^6\)

\[
n_{H}(0)\alpha / (1 - \alpha) = K_s,
\]

(11)

where \( K_s \) is the surface dissociation constant. See Fig. 2(b) for \( \alpha \) vs \( n_{H}(0)/K_s \). Since \( \alpha = 1/(1 + n_{H}(0)/K_s) \), \( \alpha \) tends to 1 (to 0) if \( n_{H}(0) \) is much smaller (larger) than \( K_s \).

We define the particle numbers \( N_i = \int_H^0 dz n_i(z) \) (i = MOH, M, OH, H) per unit area in the cell. Since the hydroxide and proton numbers due to the autoionization coincide, we have

\[
N_{OH} - N_M = N_H - \Gamma_0\alpha.
\]

(12)

It follows the overall charge neutrality condition,

\[
\int_0^H dz \rho(z) + \sigma_A = 0.
\]

(13)

In our theory, a reservoir can be attached or the system can be closed. In the latter case, the total number of the M atoms is fixed as

\[
N_M + N_{MOH} = H\bar{n},
\]

(14)

where \( \bar{n} \) is the initial density of the added base.

In Sec. III, we consider silica oxide surfaces with silanol groups AH= SiOH and see\(^6^9,15,18,20\)

\[
K_s = 10^{-7.3} \text{ mol/L} = 3.0 \times 10^{-8} \text{ nm}^3,
\]

(15)

\[
\Gamma_0 = 8.0 \times 10^{-2} \text{ nm}^2 \quad \text{(silica surface)},
\]

where \( K_s \) is very small (=0.5 \( K_b^{2/3} \)). The pH and pK values are defined by \( n_{H}^0 = 10^{-pH} \text{ mol/L} \) (in the bulk region) and \( K_s = 10^{-pK} \text{ mol/L} \). Then, \( \text{pK} = 7.3, n_{H}^0/K_s = 10^{7.3-pH}, \) and \( n_{OH}^0/K_s = 10^{pH-6.7} \) here. The value of \( \Gamma_0 \) in Eq. (15) is obtained for nonporous, fully hydrated silica, so it is large. Experimental values of \( \Gamma_0 \) strongly depend on surface preparation.\(^3^0\) It is also known that the adsorption SiOH + H\(^+\) \rightleftharpoons SiOH\(^2^-\) takes place in high acidity (low pH) conditions,\(^6,8\) leading to a zero-charge surface state at a pH about 2. See Sec. IV for analysis on ionization on carboxyl-bearing surfaces.

### B. Electric potential and Stern layers

As the electrostatic boundary condition, we may fix the potential difference between the electrodes,

\[
V = \Phi(0) - \Phi(H) + \sigma_m/C_d.
\]

(16)

We may also fix the surface charge density \( \sigma_m \) on the lower metal surface at \( z = -\ell \) (see Appendix A). In the dielectric film, the electric field is given by \( 4\pi\sigma_m/\varepsilon_d \), where \( \varepsilon_d \) is the film dielectric constant. This yields the potential change \( \Phi(-\ell) - \Phi(0) = \sigma_m/C_d \), where the film capacitance per unit area is written as

\[
C_d = \varepsilon_d/4\pi\ell.
\]

(17)

In the cell outside microscopic Stern layers (see below), \( \Phi(z) \) obeys the Poisson equation,

\[
-\varepsilon_d \partial^2 \Phi/\partial z^2 = 4\pi\rho,
\]

(18)

where \( \varepsilon_d \) is the solvent dielectric constant. The electric field is given by \( E = -\partial \Phi/\partial z \).

Generally, the electric potential can change noticeably across a microscopic Stern layer at a solid-water interface.\(^1^2,4,4^3\) We mention molecular dynamics simulations on this effect accounting for the image interaction.\(^4^4^4^8\) In our case, there are two such layers at the bottom and top. For simplicity, we assume no specific ion adsorption. Then, the ion amounts in the layers are negligibly small for small bulk ion densities.\(^1^8^8,20,4^6\) Denoting the layer thickness as \( d_0 \) at \( z = 0 \) and as \( d_H \) at \( z = H \), we assume linear relations,

\[
V_S^0 = \Phi(0) - \Phi(d_0) = (\sigma_m + \sigma_A)/C_0,
\]

\[
V_S^H = \Phi(H - d_H) - \Phi(H) = \sigma_m/C_H.
\]

(19)

For simplicity, the surface capacitances \( C_0 \) and \( C_H \) are taken to be those in the limit of small ion densities. Here, we can define the polarization \( P(z) \) microscopically such that the electric induction \( D(z) = E(z) + \pi \rho P(z) \) is continuous through the layers,\(^4^8\) where \( E(z) \) and \( P(z) \) change abruptly in the layers.\(^1^9\) We write \( D(z) \) at the bottom and the top as

\[
D(d_0) = \varepsilon_0 E(d_0) = 4\pi(\sigma_A + \sigma_m),
\]

\[
D(H - d_H) = \varepsilon_0 E(H - d_H) = 4\pi\sigma_m.
\]

(20)

These constitute the boundary conditions of the Poisson equation (18). The effective surface charge density is \( \sigma_{eff} = \sigma_A + \sigma_m \) at the bottom. Furthermore, even without applied field \( (\sigma_m = 0) \), the previous simulations\(^4^4^4^9\) have shown the presence of small potential drops at solid-water interfaces due to the anisotropy of water molecules. We neglect this intrinsic, surface effect.

The total potential difference \( V \) is now written as

\[
V = [\Phi(d_0) - \Phi(H - d_H)] + \frac{\sigma_A + \sigma_m}{C_0} + \frac{\sigma_m}{C'},
\]

(21)

where the first term arises from the mobile ions and

\[
C' = (1/C_H + 1/C_d)^{-1}.
\]

(22)
The electrostatic free energy $F_e$ appropriate at fixed $\sigma_m$ is the space integral of $DE/8\pi$ in the whole region ($-\ell < z < H$).\(^\text{50}\)

\[
F_e = \int_0^{H-d_H} dz \frac{\varepsilon_0 E^2}{8\pi} + \frac{(\sigma_A + \sigma_m)^2}{2C_0} + \frac{\sigma_m^2}{2C'},
\]

\[
= \frac{1}{2} \int_0^H dz \rho \Phi + \frac{1}{2}\sigma_N \Phi(0) + \frac{1}{2}\sigma_m V.
\]

We rewrite the integral in the first line as $|\Phi(d_H)D(d_H) - \Phi(H - d_H)D(H - d_H)|/8\pi + \int dz \Phi d/2$ and use Eq. (20).

It then follows the second line, where the integration region $d_H < z < H - d_H$ has been changed to $0 < z < H$ and $\varepsilon_N$ is related to $\rho$ by Eq. (13). Note that the integrals of $\rho$ in the Stern layers are assumed to be negligible. We also consider small changes $\rho \rightarrow \rho + \delta \rho$ and $\sigma_m \rightarrow \sigma_m + \delta \sigma_m$. The incremental change in $F_e$ is written as

\[
\delta F_e = \int_0^H dz \delta \rho \Phi + \Phi(0) \delta \sigma_A + V \delta \sigma_m,
\]

where $\delta \sigma_A = -\int_0^H dz \delta \rho(z)$ from Eq. (13) and the last term vanishes at fixed $\sigma_m$. On the other hand, at fixed $V$, the appropriate free energy is $F_e - \sigma_m V$, whose differential form is given by the first two terms in Eq. (24).

In the mean-field scheme, we neglect the image interaction between the ions and the image charges in the solid regions.\(^\text{5,30,51–53}\) In our case, they arise from the polarization in the dielectric film and the metallic boundary condition at the electrode boundaries, giving rise to fluctuation corrections to the boundary conditions (20). See further comments in Sec. VI.

In our analysis, we use the following capacitance values. (i) For our dielectric film, we assume $\varepsilon_0 = 4$ and $\ell = 1.05$ nm to obtain $C_0 = 0.0335$ F/m$^2$ from Eq. (17). On the other hand, in analysis of electrowetting, Klarman and Andelman\(^\text{14}\) assumed a much smaller value, $C_0 = 4.4 \times 10^{-6}$ F/m$^2$, for a film with $\varepsilon_0 = 2.67$ and $\ell = 5$ $\mu$m. In their case, the relation $V \simeq \sigma_m/C_0$ held nicely for not very small $V$. (ii) Supposing a silica-water interface,\(^\text{8,18–20}\) we set $C_0 = 2.9$ F/m$^2$. (iii) The metal-water capacitance\(^\text{43,47}\) has been observed in the range $0.2 - 0.5$ F/m$^2$, so we set $C_H = 0.3$ F/m$^2$. Then, $1/C_H = 0.11/C_0$ in our case. Via microscopic simulations,\(^\text{44,47,48}\) the surface capacitance for a metal-water interface has been calculated in a range of $0.05 - 0.1$ F/m$^2$ with a layer thickness about 5 $\AA$ (where water molecules are depleted).

### C. Free energy functional

We set up the Helmholtz free energy functional $F$ for a cell with $d_H \ll H$ and $d_H \ll H$ in the mean field theory. At fixed $\sigma_m$, it consists of three parts as

\[
F = F_e + F_b + F_s.
\]

At fixed $V$, we should replace $F_b$ by $F_e - \sigma_m V$. Here, $F_s$ is the contribution from the solute particles and $F_b$ is that for the surface ionization.

\[
F_b/T = \int_0^H dz \left[ \sum_i n_i \ln(n_i \lambda_i^3) - 1 \right] + \Delta_\mu M
\]

\[
+ \Delta_\mu (n_{OH} - n_{NH}),
\]

\[
F_s/T \Gamma_0 = \alpha \ln \alpha + (1 - \alpha) \ln(1 - \alpha) + \Delta_\alpha \alpha,
\]

where $\lambda_i \alpha T^{1/2}$ is the thermal de Broglie length of the particle species $i$. The $\Delta_\mu M$, $\Delta_\mu$, and $\Delta_\alpha$ are the dissociation free energies for the chemical reactions in Eqs. (1), (2), and (9), respectively, which arise from the microscopic interactions. The above form of $F_s$ has long been used in the literature.\(^\text{3,32–34,37,38}\) Where the first two terms are entropic contributions.

We define the chemical potentials of the solute particles by $\mu_i = \delta F/\delta n_i$ at fixed $\alpha$. Then, Eqs. (25)-(27) give

\[
\mu_{MOH}/T = \ln [n_{MOH} / n_{M}^{1/3}],
\]

\[
\mu_M/T = \ln [n_{M}^{1/3} / M] + \Delta_\mu - \Delta_{\mu} + U,
\]

\[
\mu_{OH}/T = \ln [n_{OH} / n_{M}^{1/3}] + \Delta_\mu - U,
\]

\[
\mu_{H}/T = \ln [n_{H} / n_{M}^{1/3}] + U,
\]

where $U(z) = e \Phi(z) / T$ is the normalized potential.

In equilibrium, we require the charge neutrality condition (12). Here, we can either assume Eq. (14) with a constant $\bar{n}$ in a closed cell or attach a reservoir to the cell with a common $\mu_{MOH}$ (see Appendix B).\(^\text{16}\) In these cases, we should minimize the grand potential,

\[
\Omega = F - h_0 (N_M + N_{MOH}) - h_1 (N_{OH} - N_{OH} + N_M - \Gamma_0 \alpha),
\]

where $h_0$ and $h_1$ are homogeneous constants. Requiring $\delta \Omega/\delta n_1 = 0$, we obtain the chemical equilibrium conditions for the mobile particles,

\[
\mu_{MOH} = \mu_M + \mu_{OH} = h_0,
\]

\[
\mu_H = \mu_{OH} = h_1.
\]

With these relations, $\Omega$ can be expressed as

\[
\Omega = F - \sum_{i=H} \mu_i N_i - \mu_H (N_{OH} - \Gamma_0 \alpha).
\]

See Appendix D for more detailed expressions of $\Omega$.

Assuming the equilibrium conditions in Eqs. (33) and (34) for $n_i(z)$, we may treat $\Omega = \Omega(\alpha)$ as a function of $\alpha$. Then, its minimization with respect to $\alpha$ gives the equilibrium $\alpha$. From Eq. (27) we obtain its derivative,

\[
\frac{1}{T \Gamma_0} \frac{d \Omega}{d \alpha} = \ln \left( \frac{\alpha}{1 - \alpha} \right) + \Delta_\alpha + \ln (\alpha / (1 - \alpha)).
\]

Using Eqs. (33) and (34) and setting $d \Omega/d \alpha = 0$, we derive the chemical equilibrium conditions (4), (5), and (11) with the dissociation constants,

\[
K_b = (\lambda_{MOH}/\lambda_{H} \lambda_{OH}) \exp (-\Delta_\mu),
\]

\[
K_w = (\lambda_{H} \lambda_{OH}) \exp (-\Delta_\mu),
\]

\[
K_s = \lambda_s^3 \exp (-\Delta_\mu).
\]

With Eq. (39) the right-hand side of Eq. (36) becomes $\ln (\alpha / (1 - \alpha) K_s)$, leading to Eq. (11) in equilibrium.

If we use $K_b$ for NaOH and $K_w$ for silica, Eqs. (37)-(39) give $\Delta_b = 8.4$, $\Delta_w = 51$, and $\Delta_s = 24$. These large sizes of
\(\Delta_w \) and \(\Delta_x \) indicate that the autoionization in water and the dissociation on a silica oxide surface are rare activation processes. On the other hand, \(\Delta_x \) is relatively small such that NaOH mostly dissociates in water.

We previously presented free energies with variable charges in mixture solvents for colloidal particles,\(^{32}\) rods,\(^{36}\) and polyelectrolytes,\(^{37}\) (without applied field). In such systems, the dissociation is governed by the composition, ionization and wetting transitions are coupled.

**D. Space-dependence of ion densities**

From Eqs. (28)-(31), \(n_{\text{MOH}} \) is a homogeneous constant. The ion densities can be expressed in terms of \(U(z)\) as

\[
\begin{align*}
    n_{\text{OH}}(z) &= n_{\text{OH}}^0 e^{-U(z)}, \\
    n_{\text{H}}(z) &= n_{\text{H}}^0 e^{-U(z)}, \\
    n_{\text{M}}(z) &= n_{\text{M}}^0 e^{-U(z)},
\end{align*}
\]

where \(n_0\) are constants with \(n_{\text{M}}^0 + n_{\text{H}}^0 = n_{\text{OH}}^0\). See Appendix B for more details on these expressions. From Eq. (18) we obtain the PB equation,

\[
d^2U/dz^2 = \kappa^2 \sinh(U).
\]

We define the Debye wave number \(\kappa\) by

\[
\kappa = (8\pi e_B n_{\text{OH}}^0)^{1/2} = 10^{-3}(n_{\text{OH}}^0/K_w^{1/2})^{1/2} \text{nm},
\]

where \(e_B = e^2/4\pi\epsilon_0 T = 7.0 \text{ Å}\) is the Bjerrum length. The inverse \(\kappa^{-1}\) is the Debye length, which is long here, but it can be shortened if we add a salt such as KCl. In such cases, \(n_{\text{OH}} \) in Eq. (42) should be replaced by the total anion density \(n_{\text{M}}^0 \) in the bulk.

For \(\kappa H \gg 1\), \(n_{\text{H}}^0\) are the bulk ion densities far from the walls as in Eqs. (6)-(8), where the charge neutrality condition holds. However, even for not large \(\kappa H\), we can use Eq. (40) with well-defined \(n_{\text{H}}^0\). Under Eq. (14) in a closed cell, \(n_{\text{H}}^0\) is determined by \(n_{\text{H}}^0 d z e^{-U} / H + n_{\text{MOH}} = \bar{n}\) (see Eq. (58)). If we attach a reservoir to the cell with a common \(n_{\text{MOH}}\), \(n_{\text{H}}^0\) in Eq. (40) are simply equal to the ion densities in the reservoir (see Appendix B).

The protons are assumed to penetrate into the Stern layers. From Eq. (19) Behrens et al.\(^{18-20}\) assumed that the ratio of its values at \(z = 0\) and \(d_0\) is given by the Boltzmann factor \(\exp(-eV_0^S/T)\), so

\[
n_{\text{H}}(0)/n_{\text{H}}(d_0) = \exp[-e(\sigma_{\Lambda} + \sigma_m)/C_0 T].
\]

However, the hydronium ions should tend to orient in a preferred direction near the surface under influence of the image charges. The resultant lowering in the free energy is of order \(T\) per ion,\(^{42}\) which leads to a larger density ratio across the Stern layer than in Eq. (43).

**E. Osmotic and disjoining pressures**

In our system, the osmotic pressure \(\Pi\) is defined in the bulk region \(d_0 < z < H - d_H\) and is given by\(^{5}\)

\[
\Pi = T \sum_i n_i \zeta_i - \frac{E_0}{8\pi} E_i^2 (z)^2,
\]

where the first term is the partial pressure of the solute particles and the second term is the \(zz\) component of the Maxwell stress tensor.\(^{50}\) In equilibrium, \(\Pi\) is a constant independent of \(z\). In fact, \(d\Pi/dz = 0\) from Eqs. (18) and (40). Here, we assume \(H > d_0 + d_H \sim 1 \text{ nm}\).

Let us treat the equilibrium (minimum) value of \(\Omega\) under Eqs. (11), (33), and (34) as a function of the cell width \(H\) in the fixed charge or the fixed potential condition. In Appendix C, we will derive the following relation:

\[
\Pi = -\frac{\partial}{\partial H}\Omega. \tag{45}
\]

A similar formula holds for the force between two colloidal particles with \(H\) being their separation distance.\(^{56}\) As will be shown in Appendix C, Eq. (45) holds when \(n_{\text{MOH}} \) or \(h_0 = \mu_{\text{MOH}}\) in Eq. (33) is fixed in the derivative. This is equivalent to fixing \(n_{\text{M}}\) or \(\Gamma_{\text{M}}\) from Eq. (4). It can be realized if we attach a reservoir to the cell. On the other hand, if the cell is closed and \(\bar{n}\) in Eq. (14) is fixed, Eq. (C5) in Appendix C and Eq. (32) lead to

\[
\Pi = -\partial \Omega / \partial H.
\]

We suppose a reservoir without applied field. The \(n_{\text{MOH}}\) in the reservoir is the same as that in the cell. Then, the disjoining pressure is the difference \(\Pi_d = \Pi - \Pi_0\), where \(\Pi_0\) is the osmotic pressure in the reservoir (see Appendix B). Using \(n_{\text{OH}}^0\) in Eq. (40), we find\(^{5,23}\)

\[
\Pi_d = T \Omega_{\text{MOH}} [2 \cosh(U) - 2 - \kappa^2 |dU/dz|^2].
\]

Thus, \(\Pi_d = -\partial(\Omega + H \Pi_{\text{M}})/\partial H\) at fixed \(n_{\text{MOH}}\). In the presence of other kind of monovalent ions, \(n_{\text{OH}}^0\) in Eq. (46) should be replaced by the total anion (cation) density \(n_{\text{M}}^0\) in the reservoir, as stated below Eq. (42).

**III. IONIZATION ON SILICA SURFACE AT LARGE WALL SEPARATION**

We consider equilibrium in a thick cell with \(H \gg \kappa^{-1}\), \(d_0\), and \(d_H\). In the middle region \(z \gg \kappa^{-1}\) and \(H - z \gg \kappa^{-1}\), the electrolyte is homogeneous with bulk ion densities \(n_{\text{M}}^0\).

**A. Basic solution for large \(H\)**

For \(H \gg \kappa^{-1}\), we impose the semi-infinite boundary condition: \(U(z) \rightarrow 0\) far from the walls. Near the bottom and the top, the profiles of the diffuse layers are given by

\[
\begin{align*}
    U(z) &= 2 \ln \left[1 - \frac{\eta e^{-eU(z-d_0)}}{1 + \eta e^{-eU(z-d_0)}}\right] \quad (\text{bottom}) \tag{47} \\
    &= 2 \ln \left[1 + \frac{\zeta e^{eU(z+d_H)}}{1 + \zeta e^{eU(z+d_H)}}\right] \quad (\text{top})
    \end{align*}
\]

From Eq. (20) the coefficients \(\eta \) and \(\zeta \) are determined by

\[
\begin{align*}
    2\eta/(1 - \eta^2) &= -(2\pi e_B / e)(\sigma_{\Lambda} + \sigma_m), \tag{48} \\
    2\zeta/(1 - \zeta^2) &= (2\pi e_B / e)\sigma_m.
    \end{align*}
\]

We define dimensionless parameters \(A_1, A_2, u,\) and \(s\) by

\[
\begin{align*}
    A_1 &= 2\pi e_B \Gamma_0/k = \Gamma_0 (\pi e_B / 2n_{\text{OH}}^0)^{1/2}, \tag{50} \\
    A_2 &= e^2 \Gamma_0 / C_0 T, \tag{51} \\
    u &= -(\sigma_{\Lambda} + \sigma_m)/e\Gamma_0 = \alpha - s, \tag{52} \\
    s &= \sigma_m / e\Gamma_0. \tag{53}
\end{align*}
\]
Then, the right-hand side of Eq. (48) is $A_1u$ and that of Eq. (49) is $A_1s$. From Eq. (20), $dU/dz$ is $2A_1u$ at $z = d_0$ and is $-2A_1s$ at $z = H - d_H$ as the boundary conditions.

In terms of these parameters, the total potential difference in Eq. (21) is rewritten as

$$\frac{e}{T}V = -g(A_1u) - A_2u + g(A_1s) + \frac{e\sigma_m}{T\Gamma},$$

(54)

where $g(x) = 2\ln(\sqrt{1 + x^2} + x)$. Then, $g(-x) = -g(x)$. In Eq. (54) the first term ($=U(d_0)$) arises from the lower diffuse layer, the second from the lower Stern layer, the third ($=-U(H - d_H)$) from the upper diffuse layer, and the last term is due to the dielectric film and the upper Stern layer with Eq. (22). Here, the Debye-Hückel theory is valid only for $|u| \ll A_1^{-1}$ at the bottom and for $|s| \ll A_1^{-1}$ at the top. For silica, we have $A_1 = 4.9 \times 10^4(K_s/n_{OH}^{0})^{1/2}$ and $A_2 = 17$. Thus, $A_1 \gg 1$ for realistic $n_{OH}^{0}$ because of large $\Gamma_0$ and small $\kappa$.

Ninham and Parsegian set pH = 4.8, $\Gamma_0 = 1$ and 0.25/ nm$^2$, and $\kappa = 1.29$ nm with a salt added. As a result, $A_1$ in Eq. (50) was of order 1 and $\kappa^{-1}$ did not exceed the Gouy-Chapman length (see Eq. (36)).

B. Profiles in the nonlinear PB regime

There appear three cases with increasing $s$: (i) $s < 0$ and $u > 0$ with $dU/dz > 0$, (ii) $s > 0$ and $u > 0$ with $U(z)$ lower near the walls than in the middle, and (iii) $s > 0$ and $u < 0$ with $dU/dz < 0$. We are interested in the nonlinear behavior of $\alpha$ in case (ii), since $\alpha \rightarrow 0$ in case (i) and $\alpha \rightarrow 1$ in case (iii).

In Fig. 3, we display $U(z)$ near the bottom for $A_1 = 1.55 \times 10^3$ (at $n_0/K_s = 10^3$ for silica), where $\alpha$ is determined for given $n_0$ and $s$. Then, $(s, \alpha) = (-0.20, 2.2 \times 10^{-5})$, $(0.90, 0.902)$, and $(1.2, 1.0)$. In the case of $s = 0.9$, $u$ is small $(0.002)$ or $(\sigma_\alpha + \sigma_m)/\sigma_m \approx -0.002$, but $A_1u = 3.1$ in the nonlinear PB regime. We shall see that this charge cancellation is a universal effect.

Let us consider the profiles of $U$ and $n_H$ at the bottom in the nonlinear PB regime $A_1u \gg 1$ with $u > 0$. The coefficient $\eta$ in Eq. (48) is close to 1 as $\eta \equiv 1 + 1/A_1u$, so

$$U(z) \approx 2 \ln[k(z - d_0 + \ell_{GC})/2],$$

$$n_H(z)/n_H^0 \approx 4\kappa^{-2}(z - d_0 + \ell_{GC})^{-2}.$$  

(55)

Here, $\ell_{GC}$ is the Gouy-Chapman length set at the bottom,

$$\ell_{GC} = (kA_1|u|)^{-1} = e/(2\pi\ell_B|\sigma_\alpha + \sigma_m|),$$

(56)

where we assume $\ell_{GC} \ll \kappa^{-1}$. The profiles change mostly on the scale of $\ell_{GC}$. In this case, $m_H(d_0)$ is larger than $n_H^0$ as

$$n_H(d_0)/n_H^0 \equiv (2A_1u)^2.$$  

(57)

The ratio $m_H(d_0)/n_H^0$ is also given by the right-hand side of Eq. (57), which is important for $n_M^{0} \approx n_{OH}^{0} \gg n_H^{0}$.

We also calculate the integral $N_H = \int_{H}^{0} dz n_H(z)$ using Eqs. (40) and (47). For $\kappa H \gg 1$, we thus obtain

$$N_H/Hn_H^0 - 1 = 2A_1\alpha/\kappa H + 2[(A_1^2)^{3/2} + (A_1^2)^{1/2} + (A_1^2)^{1/2} - 2]/\kappa.$$

(58)

The right-hand side is the correction ($\propto H^{-1}$). It can also be equated with $N_M/Hn_M^{0} - 1$ for $M^0$ and $(n_{OH}^{0} + \Gamma_0\alpha)/Hn_{OH}^{0} - 1$ for $OH^-$, where $N_M = H = n_{MOH}$ from Eq. (14) and $n_M^{0} = n_0 - n_{MOH}$ from Eq. (7). It follows $n_H^{0} \leq N_H/H$ for any $u$ and $s$. In particular, if $u \gg A_1^{-1}$ and $s \gg A_1^{-1}$, the right-hand side is $4A_1\alpha/\kappa H$ and is negligible only for $H \gg A_1\alpha\kappa^{-1}$. Thus, for $\kappa H < A_1\alpha$, the ion densities $N_H/H$ and $n_H^0$ are largely different.

C. Numerical results on $\alpha$

Use of Eqs. (40) and (43) gives the ratio of the surface proton density $n_H(0)$ to the bulk one $n_H^0$ as

$$n_H(0)/n_H^0 = \exp[g(A_1\alpha) + A_1u]$$

$$\approx [(1 + A_1^2|u|^2)^{1/2} + A_1^2u]^\alpha$$

(59)

which depends on $u$ and $n_0$. The right-hand side increases with increasing $u$ being equal to 1 for $u = 0$. In Eq. (52), $-u$ denotes the normalized, effective surface charge density at $z = 0$. Thus, for $u > 0$ ($u < 0$), the protons are more enriched (decreased) near the surface than in the bulk. From $A_1 \gg 1$, $n_H(0)/n_H^0$ can be of order only in the narrow range $|u| < A_1^{-1}$. Outside this range, it grows or decays rapidly depending on the sign of $u$ as

$$n_H(0)/n_H^0 \equiv (2A_1u)^2e^{4\kappa^2u} \gg 1$$  

($u \gg A_1^{-1}$)

$$\equiv (2A_1|u|)^2e^{-4\kappa^2|u|} \ll 1$$  

($u \gg A_1^{-1}$).  

(60)

These changes occur in the region $z < \ell_{GC}$ (see Eq. (57)).

In the surface chemical equilibrium (11), relevant is the ratio $n_H(0)/K_s$, which is close to $(K_s/n_{OH}^{0})(n_H(0)/n_H^0)$ and is calculated from Eq. (59). In the left panel of Fig. 4, it is plotted in the $u$-$n_0/K_s$ plane. From Eq. (60), it grows abruptly from small values ($<1$) to large values ($>1$) with increasing $u$ above 0. In the right panel, we show curves of $n_H(0)/K_s$ vs $u$ for several $n_0/K_s$, for which $A_1$ is indeed large.
We can see close resemblance between the left and right panels, which suggests an approximate linear relation $V \propto \sigma_m$ (see Sec. III D). In these panels, $\alpha$ increases with increasing $n_0$ in agreement with the experiment. (ii) In the middle, we write $\alpha$ vs $n_0/K_s$ where we fix $s = \sigma_m/e\Gamma_0$ at 0 and ±0.05 in (b) and $eV/T = 0$ and ±100 in (b'). These curves exhibit different behaviors with a crossover at $n_0/K_s \sim 10^4$. The curve of $\sigma_m = 0$ exhibits the power-law behavior $\alpha \propto n_0^{-2/3}$ for small $n_0$ (see Eq. (63)). (iii) In the bottom, at fixed $n_0$, we write $\alpha$ vs $s = \sigma_m/e\Gamma_0$ in (c) and $\alpha$ vs $eV/T$ in (c'), where $\alpha$ increases linearly with increasing $s$ or $eV/T$. See below for its explanation.

Note that the $\alpha$-$n_0$ relation in the 1D geometry at $s = 0$ can be used for colloidal particles with large radius ($>a^{-1}$). At $\sigma_m = 0$, Behrens and Grier calculated the curves of $\alpha$ vs pH in agreement with Fig. 6(b). At the special point $\sigma_m = n_0 = 0$, we find $\alpha = 4.7 \times 10^{-4}$ and $\sigma_x = -0.06 \mu C/cm^2$, where the latter is close to its experimental value $-0.08 \mu C/cm^2$ for silica colloidal particles in pure water.

D. Equation for $\alpha$ in nonlinear regime

In the nonlinear PB regime with $u = \alpha - s \gg A_1^{-1}$, Eqs. (11) and (60) give the following equation of $\alpha$:

$$\alpha u^2 e^{-A_1 u}/(1 - \alpha) = K_s K^2/[(2\pi\theta_0 e)^2 n_0^0]$$

$$= \left(\frac{n_0}{n_0^0}\right)^2.$$

(61)
In the second line, we set $k^2/n_e^2 = 8\pi \ell_B (n_{OH}^0)^2/K_w$ and we introduce a crossover ion density $n_c$ by

$$n_c = \left(\frac{2\pi \ell_B K_w/K_s}{1/2}\right)^{1/2}.$$  \hspace{1cm} (62)

For silica with NaOH, we find $n_c = 0.97 \times 10^{-2}$ mol/L = $1.9 \times 10^5 K_s$ from Eq. (15). For surfaces with smaller pK (much larger $K_s$), we may add HCl to increase $n_{OH}^0$ (instead of NaOH) at densities much larger than $K_s^{1/2}$, then the right-hand side of Eq. (61) becomes $K_s/n_e^2 = K_s/[2\pi \ell_B G_0^2]$.

We note that Eq. (61) reproduces the curves of $|s| < 1$ in Fig. 6(b), where we can see $\alpha < 1$ for $n_0 < n_c$. In particular, for $s = 0$ and $n_0 < n_c$, Eq. (61) gives

$$\alpha \equiv \alpha_c = (n_{OH}^0/n_c)^{2/3} = \alpha_c n_{OH}^0/K_w^{1/2}.$$  \hspace{1cm} (63)

In pure water, $\alpha_c$ tends to the following:

$$\alpha_{c0} = (K_s^{1/2}/n_e)^{2/3} = (K_s/2\pi \ell_B)^{1/3} G_0^{2/3}. $$  \hspace{1cm} (64)

For silica, we find $\alpha_{c0} = 4.7 \times 10^{-3} = 5.4/A_1$ and $U(d_0) = -7.0$, so we are already in the nonlinear PB regime at $\sigma_m = n_0 = 0$. In terms of the bulk pH, we obtain $\log_{10}[\alpha/\alpha_{c0}] \approx 2(\text{pH} - 7)/3$. Note that the relation (63) applies to large colloidal particles in the nonlinear PB regime. On the other hand, for $n_0 > n_c$, $u$ increases and the factor $e^{A_{2n}}$ becomes important.

Let us assume $n_0 \ll n_c$, for $n_c \gg K_s^{1/2}$. In Fig. 7(a), we confirm the behavior $\alpha \equiv s < 0$ in the range $0 < s < 1$, while we have $\alpha \equiv 0$ for $s < 0$ and $\alpha \equiv 1$ for $s > 1$. In (b), this behavior can be seen on a flat part of the surface of $u = \alpha - s$ in the $s = n_0/K_s$ plane. Here, self-regulated ionization is realized, where the surface charge density $\sigma_{\alpha}$ due to deprotonation nearly cancels the applied surface charge density $\sigma_m$. To be more precise, Eq. (61) yields

$$u = \alpha - s \equiv (1 - s)^{1/2}/s^{1/2} n_{OH}^0/n_c,$$  \hspace{1cm} (65)

which is much smaller than $s(\equiv s)$ for $s \gg \alpha_c$ with $\alpha_c$ being defined by Eq. (63). If $|s| < \alpha_c$, $\alpha$ becomes of order $\alpha_c$, which is consistent with Eq. (63). On the other hand, if $n_c/K_w^{1/2}$ is not large (with smaller $\Gamma_0/K_s^{1/2}$), $u$ remains not small for any $n_0$.

Finally, we need to require $A_1u \gg 1$ self-consistently, which has been assumed in setting up Eq. (61). For $|s| \gg \alpha_c$, use of Eqs. (50) and (64) gives

$$A_1u \gg (1 - s)^{1/2}/s^{1/2} (n_{OH}^0/K_s)/4 K_s^{1/2}.$$  \hspace{1cm} (66)

If $n_{OH}^0 \gtrless K_s/K_s$, $A_1u$ surely exceeds 1 for $n$ not very close to 1, including the point $s = n_0 = 0$. Thus, it generally follows the self-regulation of surface ionization for $n_0 \ll n_c$ and $0 < \sigma_m < e\Gamma_0$.

**E. Potential difference $V$ between electrodes**

In Appendix A, we will explain experimental setups at fixed $V$ and $\sigma_m$, so we should compare the results from these two boundary conditions. So far we have found that the right and left panels in Fig. 6 look similar.

In Eq. (54) the contributions to $eV/T$ are written explicitly. In the bottom panels of Fig. 7, we examine them in the range $-0.2 < s = \sigma_m/e\Gamma_0 < 1.1$ as in the upper panels. Here, $g(A_1s)$ is from the upper diffuse layer, $-g(A_1u)$ is from the lower diffuse layer, and $-g(A_1u) - A_{2u}$ includes the lower Stern layer contribution, where $n_0/K_s$ is $10^2$ in (c) and $10^4$ in (d). For positive $s$ not close to 0, the contribution from the lower diffuse layer is smaller than that from the upper

![Fig. 7](image-url)

**Fig. 7.** (a) $\alpha$ vs $s = \sigma_m/e\Gamma_0$ for $n_0/K_s = 10^2$, $10^4$, and $1.9 \times 10^5$ in range $[-0.2, 2.1]$ for silica, where $\alpha \equiv s$. (b) $u = \alpha - s$ in the $s = n_0/K_s$ plane, which is very small for $0 < s < 1$ and $n_0 \ll n_c$. The lines (blue) on the surface indicate $n_0/n_c = 0.1$ and 1. (c) Terms in $eV/T$ in Eq. (54) for $n_0/K_s = 10^2$: $g(A_1s)$ from the upper diffuse layer, $-g(A_1u)$ from the lower diffuse layer, and $-g(A_1u) - A_{2u}$ including the lower Stern layer contribution. (d) Those for $n_0/K_s = 10^4$. In (c) and (d), the PB equation can be linearized only for $g(A_1u)$ at $< 1$ at the bottom and $g(A_1s)$ at $< 1$ at the top.

![Fig. 8](image-url)

**Fig. 8.** Potential contributions in Eq. (54) (silica). Top: (a) $eV/T$ ($|s| < 0.05$) and (b) $e(V - V_d)/T$ ($|s| < 0.02$) in the $s = n_0/K_s$ plane, where $s = \sigma_m/e\Gamma_0$ and $V_d = \sigma_m/e\Gamma_0$. Bottom: Plotted are $-g(A_1u) - A_{2u}$, $g(A_1s)$, $V_d$, and their sum $V$ as functions of $s$, where $n_0/K_s$ is (c) $5 \times 10^2$ and (d) $5 \times 10^4$. See (c) and (d) of Fig. 7 for expanded plots of $-g(A_1u)$, $-g(A_1u) - A_{2u}$, and $g(A_1s)$. 

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IV. IONIZATION ON CARBOXYL-BEARING SURFACE AT LARGE WALL SEPARATION

The carboxyl surface groups undergo the dissociation (COOH ⇌ COO− + H+) at pK = 4.9 with a much smaller Γ0 in water. In their analysis, Behrens et al.18–20 used two values, Γ0 = 0.574 and 0.250 nm−2, for carboxyl-bearing surfaces. These pK and Γ0 are very different from those in Eq. (15) for silica. It is worth noting that Aoki et al.21 fabricated a carboxyl functionalized latex film with coalescence of latex particles on a Pt electrode. Analysis has also been made on other surfaces such as iron oxide ones15,18,20 which can be positively charged at low pH due to protonation.

In this section, we examine the equilibrium ionization on a carboxyl-bearing film in the 1D geometry in Fig. 1 with addition of NaOH in applied field. We set

\[ K_s = 10^{-4.9} \text{ mol/L} = 7.5 \times 10^{-6} \text{ nm}^{-3}, \]
\[ \Gamma_0 = 0.25 \text{ nm}^{-2} \] (carboxyl–bearing surface).

Here, \( K_s \) is much larger than \( K_w^{1/2} \) by 10^{−2} = 126. According to Behrens et al.18–20 the Stern capacitance at carboxyl-bearing surfaces is larger than that for silica oxide surfaces such that its presence itself can be neglected. In fact, for \( \epsilon_0 = 10 \text{ F/m}^2, A_2 \) in Eq. (51) is of order 0.1 so \( e^{A_2} \) ≈ 1 in Eq. (59) for \( |u| \leq 1 \). The other parameters are the same as in the silica case in Sec. III.

We use the PB theory in Sec. III for large \( H \). The parameter \( A_1 \) in Eq. (50) becomes \( A_1 = 1.5 \times 10^3 \left( n_0/(n_c^{0.4}) \right)^{1/2} \).

In Eq. (61) we neglect the Stern factor \( e^{A_2} \) and assume \( u = \alpha - s \approx A_1^{-1} \) to obtain

\[ \alpha^2 / (1 - \alpha) \approx (n_0/\epsilon n_c)^2, \] (68)

where \( n_c = 1.9 \times 10^{-5} \text{ mol/L} = 1.5 K_s \) from Eq. (67). It is smaller than that for silica by 500^−1. At the special point \( n_0 = \sigma m = 0 \), our numerical analysis indicates \( U(0) = -8.32 \) and \( \alpha = 0.030 = 32/A_1 \), where the latter nearly coincides with \( \sigma, \Gamma_0 \) in Eq. (64). We are in the nonlinear PB regime at this point.

In Fig. 9, we show \( \alpha \) in (a) the \( s - n_0/K_s \) plane and in (b) the \( eV/T - n_0/K_s \) plane, as in (a) and (a′) of Fig. 6. Here, \( \log_{10}(n_0/K) = \text{pH} - 9.1 \). These look similar as in Fig. 6, indicating the linear relation \( V \approx \sigma C \) except for small \( \sigma m \).

In (c), \( \alpha \) vs \( n_0/K_s \) is plotted for \( s = 0 \) and ±0.1, as in Fig. 6(b). Here, \( \alpha \) approaches 1 for \( n_0 \sim 6K_s \sim 4n_c \). The curve at \( \sigma_m = 0 \) coincides with that calculated by Behrens and Grier.20 In (d), we display \( \alpha \) vs \( s \) for \( n_0/K_s = 10^{-3}, 0.1, \) and 1 in the range \(-0.2, 1.1 \). As in Fig. 7(a), we can again find the linear behavior \( \alpha \approx s \) for \( 0 < s < 1 \) for \( n_0 < n_c \).

In Fig. 10, displayed is (a) \( u = \alpha - s \) in the \( s - n_0/K_s \) plane for carboxyl-bearing surface, which is very small for \( 0 < s < 1 \) and \( n_0 < 0.1n_c \sim 0.15K_s \), as in Fig. 7(b). The lines (blue) on the surface indicate \( n_0/n_c = 0.1 \) and 1. (b) The terms in \( eV/T \) in Eq. (54) are shown for \( n_0/K_s = 10^2 \), where they are \( g(A_{1s}) \) from the upper diffuse layer and \( -g(A_{1u}) \) from the lower diffuse layer for \( n_0/K_s = 0.1 \) and 10^{-3}.

V. IONIZATION AND DISJOINING PRESSURE AT SMALL WALL SEPARATION

The disjoining pressure \( \Pi_d \) in Eq. (46) is a measurable quantity.12–14 It has been calculated between ionizable
surfaces at small separation.\textsuperscript{16,17,23} Here, attaching a reservoir, we examine how $\Pi_d$ and $\alpha$ depend on $H$ and $\sigma_m$ with NaOH added at a density $n_0$. We consider the Stern layers, so we define the effective cell thickness by

$$H' = H - (d_0 + d_H),$$

(69)

where $d_0$ and $d_H$ are of order 5Å. There is a sizable range of $H' < \kappa^{-1}$ for not large $n_0$. Using Eqs. (11) and (40), we integrated the PB equation in the region $0 < z - d_0 < H'$ for each given $n_0$ and $\sigma_m$. The parameters are those for silica oxide surfaces in Figs. 11-16, but those for carboxyl-bearing surfaces are also used in Fig. 17(b). For simplicity, we neglect the van der Waals interaction.\textsuperscript{1,2,4}

A. Results without applied field ($s = 0$)

First, we assume no applied field ($s = 0$). Because $dU/dz = 0$ at $z = H - d_H$, our $H'$ corresponds to a half of the cell thickness in the symmetric case.\textsuperscript{16,23} For thick cells with $H' > \kappa^{-1}$, it follows a well-known result,\textsuperscript{1,3,29}

$$\Pi_d \approx 64 T n_0^0 \exp(-2xH').$$

(70)

Ninham and Parsegian\textsuperscript{16} derived the power-law behavior $\Pi_d \propto H'^{-1/2}$ as $H \to 0$ between symmetric ionizable walls. From analysis in Appendix E, their asymptotic behavior appears for $H' \ll \ell_{GC}$ in the case $A_1^{-1} \ll \alpha \ll 1$. Here, $\ell_{GC} = (\kappa A_1)^{-1}$ is the Gouy-Chapman length in Eq. (56) shorter than $\kappa^{-1}$ in the nonlinear PB regime. In this asymptotic case the normalized potential values $U_0 = U(d_0)$ and $U_H = U(H - d_H)$ at the two ends are given by

$$U_H - U_0 \approx A_1 \alpha k H' = H' / \ell_{GC} \ll 1,$$

(71)

and $\exp(-U_0) \approx 4 A_1 \alpha / k H' \gg 1.$

(72)

From Eq. (11) and (46), $\Pi_d$ and $\alpha$ behave as

$$\Pi_d \approx T n_0^0 \exp(-U),$$

(73)

$$\alpha \approx (K_0 H' / \Gamma_0 n_0^0)^{1/2} \ell_{GC},$$

(74)

where we set $n_0^0 = K_0 n_0^0$. With other added ions, however, Eqs. (73) and (74) should be changed appropriately (see the comments below Eqs. (42) and (46)).\textsuperscript{16,23} In addition, the inequality $\alpha \ll 1$ holds for

$$H' \ll (\Gamma_0 K_s (\ell_{GC}^2 / n_0^0)^2.$$

(75)

For silica oxide surfaces, we have $\Gamma_0 / K_s \approx 10^8$ nm, so Eq. (75) can well be satisfied together with Eq. (71).

On the other hand, when $\ell_{GC} \ll H' \ll \kappa^{-1}$ in the nonlinear PB regime, we find another regime (the Gouy-Chapman regime\textsuperscript{29}), where $U_0$ and $\alpha$ remain nearly at constants but $U_H$ strongly depends on $H'$. That is,

$$\exp(-U_0) \approx (2 A_1 \alpha)^2,$$

(76)

$$\exp(-U_H) \approx (\kappa / k H')^2.$$
FIG. 14. $\alpha$ (top) and $u = \alpha - s$ (bottom) in the $H'/\ell_B$-$s$ plane for silica, where $n_0/K_s$ is (a) 10 (left) and (b) $10^3$ (right). For not small $s > 0$, $\alpha$ is insensitive to $H'$ larger than $5\ell_B$. Lines of $u = (A_1H')^{-1} > 0$, $u = 0$, and $u = -(A_1H')^{-1} < 0$ (from above) are written on the surfaces of $u$ (blue lines). Below (above) the middle blue line ($u = 0$), $u$ is negative (positive).

Thus, $e^{U_H-U_0} \sim (H'/\ell_{GC})^2 \gg 1$. The $P_d$ behaves as

$$P_d \propto T^0_{OH} e^{-U_H} = \pi T/[2\ell_B(2H')^2],$$

which is independent of $n_0$ and $\alpha$. In the previous theories, the behavior (78) was not found, because they adopted parameters yielding $\ell_{GC} \gg \kappa^{-1}$ with a salt added (see the last paragraph of Sec. III A).

In Fig. 11, we show (a) $\Pi_d$, (b) $\alpha$, (c) $U_0$, and (d) $U_0 - U_H$ as functions of $H'$ in the range $\ell_B < H' < 30\ell_B < \kappa^{-1}$ without applied field ($s = 0$) for silica oxide surfaces. We set $n_0/K_s = 10^{-2}, 10,$ and $10^3$, where $\kappa\ell_B \times 10^3 = 0.72, 1.6$, and 5.0 and $A_1 \times 10^{-3}$ is 34, 15, and 4.9, respectively. In these cases, $A_0\alpha$ remains considerably larger than 1 for $H' > \ell_B = 7\text{Å}$ from Eq. (63). We can clearly see the crossover between the two-power-law regimes at $H' = \ell_{GC}$ as follows. In (a), $\Pi_d$ behaves as in Eqs. (73) and (78). In (b), $\alpha$ decays as $\sqrt{H'}$ for small $H'$ and is a small constant for larger $H'$. In (c), $U_0$ satisfies Eqs. (72) and (76) in the range $[-9, -7]$, tending to be independent of $n_0$ for $H' < \ell_{GC}$. In (d), $U_0 - U_H$ behaves in accord with Eqs. (71) and (77).

In Fig. 12, we display the profiles of $U(z)$ without applied field for $n_0/K_s = 10^{-2}, 10,$ and $10^3$. In (a), we set $H' = 200\ell_B < \kappa^{-1}$, then $H' > \ell_{GC}$ with $\ell_{GC}/\ell_B = 6.7, 30,$ and 93, respectively. In (b), we set $H' = 3.3\ell_B$ to realize $H' < \ell_{GC}$ with $\ell_{GC}/\ell_B = 440, 87,$ and 10, where the diffuse layers at the bottom and top walls largely overlap.

B. Results with applied field

Next, we apply electric field by varying $s = \sigma_m/e\Gamma_0$ for $\kappa H' < 1$. In Fig. 13, $\Pi_d$ is displayed as a function of $H'$ parameters yielding $\ell_{GC} \gg \kappa^{-1}$ with a salt added (see the last paragraph of Sec. III A).

FIG. 15. Results for silica with $\kappa H' = 0.08$ and $n_0/K_s = 10^3$, where $\kappa = 2.2 \times 10^{-3}$ nm$^{-1}$. Displayed is $U(z)$ in the range $0 < z - d_0 < H'$ for (a) $s = 0.9$, $\alpha = 0.875$, and $\ell_B^2\Pi_d/T = -0.0580$ and (b) $s = 1.2$, $\alpha = 1.0$, and $\ell_B^2\Pi_d/T = -0.951$. Plotted also is $n_{OH}(z) = n_{OH}^0 e^{-U_0(z)}$ near the bottom in units of mm$^{-1}$ (inset). (c) Screening fraction $1 - b/|u|$ and $u$ (inset) vs $s$. Screening is very weak for $s < 1.1$. (d) $\ell_B^2\Pi_d/T$ and $\alpha$ (inset) vs $s$, where $\Pi_d < 0$ for most $s$.
and $s$. We fix $n_0/K_s$ at 10 and $10^3$, where $A_1$ is $1.5 \times 10^4$ and $1.5 \times 10^5$, respectively. The $\Pi_d$ is positive around the line of $s = 0$ but is mostly negative. This is natural because the surface charge densities at the two ends have the same sign only for $0 < s < \alpha$. If $kH' < 1$, we find $\Pi_d > 0$ holds only for $|s| < \alpha$, where $\alpha$ is the value of the degree of ionization at $s = 0$. This width of $s$ is of order $\alpha \sim 10^{-3}$ in (a) and $10^{-2}$ in (b) from Eq. (63). In addition, for not small $|s|$, $\Pi_d$ drops to negative values with large amplitude with decreasing $H'$ due to partial screening (see below).

In Fig. 14, we plot $\alpha$ and $\mu = -\alpha/s$ for $1 < H'/\ell_B < 10^2$ and $-0.2 < s < 1.2$, where $n_0/K_s = 10$ (left) and $10^3$ (right). For $H' \geq \ell_B$, $\alpha$ is nearly independent of $H'$ in the upper panels and $\mu$ is very small for $0 < s < 1$ in the bottom panels. Thus, the self-regulation (found for $H' \gg k^{-1}$ in Sec. III) is operative even for small $H'(\geq \ell_B)$. We also write the lines of $u = 0$ and $\pm (A_1H'\kappa)^{-1}$. We have $H' > \ell_B$ outside them. These three lines are closely located because of large $A_1$, which is $1.5 \times 10^4$ (left) and $1.5 \times 10^5$ (right). Indeed, on the flat area in the left, we have $-0.01 < u < -0.001$ and $A_1|u| > 15$.

In Fig. 15, we show typical profiles of $U$ for $u$ and $s > 0$ with $H' = \ell_B = 0.08/k$, which exhibit a negative slope far from the walls. Such profiles can appear for $\Pi_d < 0$, so we define a dimensionless number $b$ by

$$b = (-\Pi_d/2\pi T_B)^{1/2}/\Gamma_0. \quad (79)$$

Then, $\Pi_d/\ell_B = -4\Lambda_b^2b^2$. The slope of $U$ is $-2A_1b\kappa$ and the corresponding electric field is $4\pi T_B\Gamma_0/b\ell_B$ far from the walls. Here, the anions (OH$^-$) are accumulated at the bottom and the cations (M$^+$ and H$^+$) at the top, but their screening of the surface charges is only partial. The accumulated ion numbers $N_i = \int dz n_0(z)$ satisfy

$$N_{OH} = \Gamma_0|u| - b, \quad (80)$$

$$N_{H} + N_M = \Gamma_0(s - b), \quad (81)$$

which are consistent with Eq. (12). The degree of screening (screening fraction) is given by $1 - b/|u|$ at the bottom and by $1 - b/s$ at the top. It is 0 with no screening (with no diffuse layer) and is 1 for complete screening.

In Fig. 15, at $n_0/K_s = 10^3$, we find $s = 0.9$, $\alpha = 0.875$, and $b = 0.0245 = 37/A_1$ in (a) and $s = 1.2$, $\alpha = 1.0$, and $b = 0.099 = 150/A_1$ in (b). Thus, $1 - b/|u| = 0.02$ in (a) and 0.5 in (b). In fact, $n_{OH}(z)$ is very small in (a) but is appreciable in (b) (inset). In (c), we show $1 - b/|u|$ vs $s$ in the range $0.6 < s < 1.2$, which is very small for $s < 1.1$ but grows abruptly for $s > 1.1$. In $s < 1.1$, there is almost no screening at the bottom and the screening fraction at the top is $\alpha/s$. In (d), we plot $\Pi_d$ and $\alpha$ in the range $-0.2 < s < 1.2$. In accord with Fig. 13, $\Pi_d$ is positive only in a narrow range of $|s|(< 0.2 < s < 1.2)$. The region of $\Pi_d > 0$ is widened with increasing $n_0$.

The region of $\Pi_d > 0$ is widened with increasing $n_0$. See the two panels in Fig. 13, where $n_0/K_s = 10$ and $10^3$. In Fig. 16, this is more apparent for $n_0/K_s = 10^4$ with $H' = \ell_B = 0.25/k$, where $n_{OH} \cong n_{OH}^0 \gg n_H^0$. In (a), $\Pi_d$ is about $0.05T_B^2 \sim 250T_Bn_0$ for $0 < s < 1$, where $U(z)$ is negative with a maximum about $-6.0$ and the ions in the cell are mostly M$^+$. However, $\Pi_d$ becomes negative abruptly for $s > 1$. In (b), the profile of $U(z)$ exhibits a changeover across $s = 1$ at this $n_0$. For $s = 0.4$, $E$ vanishes at the maximum point. However, once $\Pi_d < 0$, unscreening is significant at the bottom; in fact, $(u_1 - b/|u|) = (-0.012,0.10)$ for $s = 1.0$ and $(-0.10,0.24)$ for $s = 1.1$. The characteristic features of these behaviors are unchanged even for $n_0/K_s = 10^5$ (not shown here).

The screening should be easier for larger $n_0$. This is confirmed in Fig. 17, where plotted is $1 - b/|u|$ vs $n_0/K_s$ at fixed $s$ for (a) silica oxide surfaces and (b) carboxyl-bearing surfaces. Here, $H' = \ell_B$ in (a) and $50\ell_B$ in (b). The $K_s$ and $\Gamma_0$ in the two systems are very different in Eqs. (15) and (67). Nevertheless, we can see significant unscreening at relatively small $n_0$ in the two systems. In addition, the changeover from unscreening to screening with increasing $n_0$ is nearly discontinuous for $0 < s < 1$ (from $b \approx s - \alpha$ to $b \approx 0$), while it is gradual for $s > 1$.

### C. Theory of partial screening in thin cells

We finally present some analytic results on the partial screening. See Appendix E for their derivations. With $b \gg A_1^{-1}$, we introduce a characteristic length $\ell_w$ by

$$\ell_w = (2A_1b)^{-1}k^{-1} = (4\pi T_B\Gamma_0)^{-1}, \quad (82)$$

which is of the same order as $\ell_B$ in Eq. (56) for $|u| \sim b$. If we assume $U(H - d_H) = U_T < 0$ and $[U_H] \gg 1$, $U(z)$ near the top is well approximated by

$$U(z) \equiv U_H + w + 2\ln(1 + a_H - a_{He}e^{-w}) \quad (top), \quad (83)$$

where $w = (H - d_H - z)/\ell_w$ and $a_H = s/2b - 1/2$. The last term is zero at $w = 0$ and tends to $2\ln(1 + a_H)$ for $w \gg 1$, so the profile changes on the scale of $\ell_w$. This formula excellently describes the profiles in (a) and (b) of Fig. 15 and those in Fig. 16(b) near the top. The interior electric field is a constant for $\ell_w \sim H'$. For the profiles in Fig. 15(a) and those of $s = 1$ and 1.1 in Fig. 16(b), we have $b \approx |u|$, so Eq. (83) can be used even at the bottom.

For the profile in Fig. 15(b), the diffusive layer near the bottom gives $b \approx 0.5|u|$. In this partial screening, the profile at the bottom is well approximated by

$$U(z) \equiv U_0 - s - 2\ln(1 + a_0 - a_{He}e^{-w}) \quad (bottom), \quad (84)$$

where $U(d_0) = U_0$. As $s = 0$, $s = (z - d_0)/\ell_w$, and $a_0 = |u|/2b - 1/2$. For the profile in Fig. 15(b), Eqs. (83) and (84) should coincide far from the walls, so we require

$$H'/\ell_w \geq U_0 - U_H - 2\ln[(1 + a_0)(1 + a_H)] \equiv 4\ln(4A_1b) + \ln\left[\frac{|u| - b(s - b)}{|u| + b(s + b)}\right]. \quad (85)$$

The right-hand side can much exceed 1 for $A_1b \gg 1$. For (b) in Fig. 15, Eq. (85) is nearly exact.

### VI. SUMMARY AND REMARKS

We have examined ionization on a dielectric film in water in applied field. In the geometry in Fig. 1, the surface can be negatively charged with proton desorption. From the mass
action law, the degree of dissociation $\alpha$ is determined by the ratio of the proton density close to the film $n_\text{ff}(0)$ and the dissociation constant $K_s(=10^{7.8}$ mol/L). We have added NaOH at a density $n_0$ in water\(^{27}\) to decrease $n_\text{ff}(0)$. Main results are summarized as follows.

(i) In Sec. II, we have presented the free energy $F$, depending on the solute densities $n_s$ and the degree of ionization $\alpha$, where the electrode charge density $\sigma_m$ or the potential difference $V$ is fixed. The contributions from the ionizable film and the Stern layers have been included. Minimization of the corresponding grand potential $\Omega$ yields equilibrium conditions including the mass action laws. The derivative of the equilibrium $\Omega$ with respect to the cell width $H$ yields the osmotic pressure $\Pi$.

(ii) In Sec. III, we have assumed $H \gg \kappa^{-1}$. Analysis has been made on silica oxide films with $pK = 7.3$ in the nonlinear PB regime, where the Gouy-Chapman length $\ell_{GC}$ is shorter than $\kappa^{-1}$. We have obtained a simple equation for $\alpha$ in Eq. (61) for given $\sigma_m$ and $n_0$. As in Fig. 7(b), we have found remarkable self-regulation behavior $\alpha \equiv s = \sigma_m/\ell\Gamma_0$ for $0 < s < 1$ and $n_0 \ll n_c$, where $\Gamma_0$ is the areal density of the ionizable groups and $n_c$ is a crossover density. From Eq. (62), we find $n_c = 10^{-2}$ mol/L for silica oxide surfaces.

(iii) In Sec. IV, we have presented results using the parameters of carboxyl-bearing surfaces with $pK = 4.9$. General trends are common to those for silica oxide surfaces as in Figs. 8 and 9, but numerical factors are very different. For example, we have $n_c = 2 \times 10^{-5}$ mol/L.

(iv) In Sec. V, we have presented analysis for small $H' = H - (d_0 + \delta H)$ with a reservoir attached. Without applied field, the disjoining pressure $\Pi_d$ is proportional to $\sqrt{H'}$ for $H' < \ell_{GC}$ and to $(H')^{-2}$ for $\ell_{GC} < H' < \kappa^{-1}$. In applied field, the self-regulation ($\alpha \equiv s$ for $0 < s < 1$) holds even for $\ell < H' < \kappa^{-1}$. We have also shown that the surface charges can be screened only partially for not small $s$. For silica oxide surfaces, $\Pi_d$ is mostly negative for $n_0/K_s \leq 10^5$ in Figs. 13 and 15(d), but it assumes a large positive value in the range $0 < s < 1$ for $n_0/K_s = 10^4$ in Fig. 16. Similar results follow for hydroxyl-bearing surfaces as in Fig. 17. We have derived analytic expressions for the potential profiles in partial screening in Eqs. (83) and (84).

(v) In Appendix A, we have examined the experimental method of imposing the fixed charge condition. In Appendix C, we have derived the expressions for the osmotic and disjoining pressures. In Appendix D, we have derived the expressions for the surface free energy for ionizable surfaces in applied field.

We make some remarks.

1. We have neglected the effect of the image charges on the mobile ions near the surfaces $^{5,30,51–53}$ and the interaction among the ionized groups.$^5$ However, these effects can substantially change the surface dissociation behavior. Thus, they should be examined in future.

2. There are a variety of ionizable surfaces with very different parameters ($K_s$ and $\Gamma_0$)$^{15,18–22}$ under strong influence of ions. We have examined dissociation with small $K_s$, where the autoionization of water comes into play. The charge regulation has been controlled by the amount of NaOH. If $K_s$ is much larger, we may add HCl to increase the bulk proton density $n_\text{ff}$. We can also add KCl to increase $\kappa$, as discussed below Eqs. (42), (46), and (74). Also partial screening appears in many situations, which should be studied systematically.

3. We should study dynamics of surface ionization in nonstationary electric field. We note that the deprotonation on a silica-water interface takes place very slowly as rare thermal activations.$^59$

4. There are a number of nonequilibrium situations with chemical reactions,$^{28,60}$ where phase changes can take place. Such problems mostly remain unexplored. For example, electrowetting$^{54,55}$ has been studied without chemical reactions.

**ACKNOWLEDGMENTS**

This work was supported by KAKENHI No. 25610122. R.O. acknowledges support from the Grant-in-Aid for Scientific Research on Innovative Areas Fluctuation and Structure (Grant No. 25103010) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. We would like to thank Junpei Yamanaka for valuable discussions.

**APPENDIX A: REALIZATION OF CONSTANT CHARGE BOUNDARY CONDITION**

In Fig. 1, a battery has been used to produce an equilibrium electrolyte state at a given potential difference $V$. If it is disconnected, the surface charge density $\sigma_m$ (at the lower metal surface) becomes fixed.

As illustrated in Fig. 1, we further connect a small external condenser with a capacitance $C_\text{ex}$ to the electrodes. The potential difference of the capacitor is given by

$$V_\text{ex} = Q_\text{ex}/C_\text{ex},$$  \hspace{1cm} (A1)

where $Q_\text{ex}$ is the initial charge. After this connection, the surface charge density and the potential difference of the electrodes are changed as $\sigma_m \rightarrow \sigma_m + \Delta \sigma_m$ and $V \rightarrow V + \Delta V$. Then, the capacitor change is changed by $-S_0\Delta \sigma_m$, where $S_0$ is the surface area of the electrodes. If the potential equilibration is attained, we have

$$V + \Delta V = [Q_\text{ex} - S_0\Delta \sigma_m]/C_\text{ex}. \hspace{1cm} (A2)$$

In the limit of small $\Delta \sigma_m$, we may set $\Delta V = \partial \sigma_m/\partial V$ as the differential capacitance of our system (per unit area). Then, Eq. (A2) yields

$$\Delta \sigma_m = (V_\text{ex} - V)/[S_0/C_\text{ex} + 1/C_\text{diff}], \hspace{1cm} (A3)$$

where the second line holds for $C_\text{ex} \ll S_0/C_\text{diff}$. Therefore, for sufficiently small $C_\text{ex}$ at fixed $V_\text{ex}$, $\Delta \sigma_m$ depends only on the initial $V$ of our system and remains fixed independently of the subsequent physical and chemical processes in the cell.
APPENDIX B: BULK ION DENSITIES IN TERMS OF \( n_{\text{MOH}} \)

In Eq. (40) we can assume the relation,

\[
n^0_M + n^0_H = n^0_{\text{OH}},
\]

without loss of generality by shifting the origin of \( U(z) \) appropriately (\( U \to U + \text{constant} \)). Then, we obtain Eq. (41). From the chemical equilibrium conditions (4) and (5), \( n^0_H \) and \( n^0_M \) are expressed as

\[
n^0_H = K_w/n^0_{\text{OH}}, \quad n^0_M = K_{\text{p MOH}}/n^0_{\text{OH}},
\]

From Eqs. (B1) and (B2), \( n^0_{\text{OH}} \) is given by

\[
n^0_{\text{OH}} = (K_w + K_{\text{p MOH}})^{1/2}.
\]

The density \( n_0 \) of M atoms in Eq. (7) is expressed as

\[
n_0 = n_{\text{MOH}}(1 + K_w/n^0_{\text{OH}}).
\]

For \( kH \gg 1 \), \( n^0_i \) coincide with those in Eqs. (6)-(8).

We can attach a reservoir with the same \( n_{\text{MOH}} \) as that in the cell. Then, the reservoir densities of \( H^+ \), \( OH^- \), and \( M^+ \) are given by \( n^0_H \) and \( n^0_{\text{OH}} \) and \( n^0_M \) in Eqs. (B2) and (B3). To derive Eq. (46) we note that the reservoir osmotic pressure is written as

\[
\Pi_0^i = T \sum_i n^0_i = T(n_{\text{MOH}} + 2n^0_{\text{OH}}).
\]

APPENDIX C: FORCE BETWEEN PARALLEL WALLS

We suppose two equilibrium states in the geometry in Fig. 1, where the cell length is \( H \) in one state and \( H + \delta H \) in the other slightly elongated one. The water density and the temperature are common. All the quantities are independent of the lateral coordinates \( x \) and \( y \). The grand potentials \( \Omega \) and \( \Omega' \) per unit area are defined in the two states from Eq. (32) or Eq. (35). We calculate the difference \( \delta \Omega = \Omega' - \Omega \) for small \( \delta H \).

In the elongated state, the quantities are denoted with a prime and the space coordinate is written as \( z' \), where \( n'_i(z') \) are the densities and \( \alpha' \) is the degree of ionization. We impose \( \sigma'_m = \sigma_m \) at fixed charge and \( V' = V \) at fixed potential difference. We assume a mapping relation between the positions \( z' \) and \( z \) given by

\[
z' = z + w(z), \quad \sigma_m = \sigma_m \quad \text{at} \quad \delta \alpha = \alpha' - \alpha.
\]

The mapping (C1) yields \( d/dz = (1 + w')d/dz' \) and \( n^0_{H + \delta H} d'z' = n^0_{H} dz(1 + w') \), with \( w' = dw/dz \). Then, from \( \varepsilon_0 dE'/dz' = 4\pi\rho'(z') \), the deviation \( \delta E = E'(z') - E(z) \) is related to \( \delta \rho = \rho'(z') - \rho(z) \) as

\[
\varepsilon_0 \frac{d}{dz} \delta E = 4\pi (w' \delta \rho + \delta \rho).
\]

to linear order. From Eq. (23) the deviation in the electrostatic free energy, \( \delta F_e = F_e' - F_e \), is calculated as

\[
\delta F_e = \int dz w' \left[ \frac{\varepsilon_0}{8\pi} E^2 + \rho \Phi \right] + \int dz \Phi \delta \rho + \Phi(0)\delta\sigma_A + V\delta\sigma_m,
\]

where the first term arises from the cell elongation and the other terms coincide with those in Eq. (24). Similarly, the elongation contribution to \( F_b \) in Eq. (26) is given by \( \int dz w' f_b \), where \( f_b \) is the bulk free energy density in \( F_b = \int dz f_b \). From Eq. (32) or Eq. (35), we find

\[
\delta \Omega = -\int dz w' \Pi - (n_M + n_{\text{MOH}})\delta h_0 = -\Pi H - (n_M + n_{\text{MOH}})h_0,
\]

where \( \delta h_0 = h_0' - h_0 \) and \( \Pi \) is given in Eq. (44). Since \( \Pi \) is a constant, we obtain the second line. Note that Eq. (C5) holds both at fixed \( \sigma_m \) and fixed \( V \).

The 1D theory in this appendix can be extended in various 3D situations. For example, we can calculate the solvent-mediated interaction between colloidal particles in a mixture solvent. The 3D mapping \( x'_s = x_s + w_h \) has been used in elasticity theory. Moreover, we can use it to derive the reversible part of the stress tensor for various fluids (including near-critical fluids, liquid crystals, and electrolytes).

APPENDIX D: CALCULATION OF SURFACE FREE ENERGY

We calculate \( \Omega \) in Eq. (35) at fixed \( \sigma_m \) and \( n^0_{\text{OH}} \) using Eqs. (18), (33), and (34). It is rewritten as

\[
\Omega = -\int dz \left[ T \sum_i n_i + \frac{\varepsilon_0}{8\pi} E^2 - \frac{\sigma^2}{2C_O} - \frac{\sigma^2}{2C_{\text{tot}}} + F_s \right. \right. + T \delta \alpha \ln [n_H(0)l_H^1] + \Phi(0) - \Phi(H - d_H)] \sigma_m],
\]

where \( C_{\text{tot}}^1 = C_{\text{H}}^1 + C_{\text{H}}^1 + C_{\text{H}}^1 \). At fixed \( V \), we should subtract \( Vs\sigma_m \) from the right-hand side.

We assume a thick cell with \( kH \gg 1 \), where \( n_i \to n^0_i \) and \( E \to 0 \) far from the walls. Then, using Eqs. (40) and (47), we can rewrite Eq. (D1) as

\[
\Omega = -H\Pi_0' + \gamma_H + \gamma_0 + \sigma^2/2C_{\text{tot}},
\]

where \( \Pi_0' \) is the reservoir osmotic pressure in Eq. (B5). The \( \gamma_H \) is the surface free energy from the upper diffuse layer (without surface ionization) given by

\[
\gamma_H/T = \left[ 1 - (A_1^1 s^2 + 1)^{1/2} / k/\ell_B + g(A_1 s)\sigma_m / e \right],
\]

where \( g(x) = 2\ln[1 + x^2 + x] \). The \( \gamma_0 \) is that of the lower surface and the difference \( \Delta \Omega = \gamma_0 - \gamma_H \) is the contribution due to the surface ionization of the form

\[
\Delta \Omega \quad T_0 = \frac{2}{A_1} \left[ (A_1^1 s^2 + 1)^{1/2} - (A_1^1 s^2 + 1)^{1/2} \right] + F_s \quad T_0
\]

\[
+ \alpha \ln [n_H(0)A_1^1] - s[g(A_1 s) + g(A_1 s)] - A_2^2 / 2 \sigma. \quad \text{(D4)}
\]

This quantity is important for wetting on ionizable surfaces.
We can integrate Eq. (E1) in the following form:

\[
\int_{z_1}^{z_2} k^{-2} (dU/dz)^2 \, dz = e^{-U(z)/kT} - e^{-U_H/kT}, \tag{E1}
\]

\[
(2A_1\alpha)^2 \int_{z_1}^{z_2} e^{-U_H/kT} - e^{-U_H/kT} \, dz. \tag{E2}
\]

We can integrate Eq. (E1) in the following form:

\[
\int_{U_0}^{U_H} \left( \int_{z_1}^{z_2} k^{-2} \, dz \right) \, dU = \frac{2e^{U_H/kT}}{2 + e^{U_H/kT}} - \frac{e^{U_H/kT}}{2 + e^{U_H/kT}} \tag{E3}
\]

where we use \( \int_{z_1}^{z_2} \, dz = (z_2 - z_1) = \ell_{\text{dc}} \) by setting \( y = U_H - U \). We define

\[
q(z) = \exp[U_H - U(z)] - 1, \tag{E4}
\]

where \( q(0) = 0 \) and \( q(d_0) = (2A_1\alpha)^2 \exp(U_H) \). There are two cases. If \( q < 1 \), we can set \( \frac{1}{\sqrt{q}} \equiv (U_H - U_H) \leq 1 \) in Eq. (E3) to obtain \( H_H \ll \ell_{\text{dc}} \) and Eqs. (71)-(74). On the other hand, if \( q > 1 \), we can set \( \frac{1}{\sqrt{q}} \equiv \pi/2 \) to obtain \( H_H \gg \ell_{\text{dc}} \) and Eqs. (76)-(78).

Calculations of partial screening.

We explain the partial screening in Fig. 15 with \( s > 0 \) and \( u < 0 \). In terms of \( b \) in Eq. (79), the PB equation in Eq. (46) becomes

\[
2 \cosh(2U_H) - 1 = 2A_1^2(b^2 - b^2), \tag{E6}
\]

\[
\cosh(2U_H) - 1 = 2A_1^2(s^2 - b^2). \tag{E7}
\]

If \( U_H < 0 \) and \( |U_H| \gg 1 \), we can replace \( \cosh(U_H) - 1 \) by \( e^{U_H/2} \) in Eq. (E5) near the top. It follows Eq. (83). Integration of \( n_{1H}(z)/n_H = n_M(z)/n_0 = e^{-U_H/kT} \) near the top can be performed to give Eq. (81). On the other hand, if \( U_H \gg 1 \), we can replace \( \cosh(U_H) - 1 \) by \( e^{U_H/2} \) near the bottom. Then, Eq. (84) is obtained and integration of \( n_{1H}(z)/n_H = e^{U_H/kT} \) near the bottom yields Eq. (80).


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As the Stern potential drop, we find the expression
\[ V_S = \frac{4\pi}{\varepsilon_0} \int_{d_0}^{d} dz \left[ P_b - P(z) \right] \]
where \( P_b = (\varepsilon_0 - 1)E(d_0)/4\pi \) is the bulk polarization close to the bottom Stern layer. Here, \( P(z) \) can be nonvanishing even for \( P_b = 0 \) due to the molecular orientation, leading to an intrinsic potential drop.


