

Coulombic Surface-Ion Interactions Induce Nonlinear and Chemistry-Specific Charging Kinetics

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(Received 4 November 2022; accepted 15 December 2022; published 3 February 2023)

While important for many industrial applications, chemical reactions responsible for the charging of solids in water are often poorly understood. We theoretically investigate the charging kinetics of solid-liquid interfaces and find that the time-dependent equilibration of surface charge contains key information not only on the reaction mechanism, but also on the valency of the reacting ions. We construct a nonlinear differential equation describing surface charging by combining chemical Langmuir kinetics and electrostatic Poisson-Boltzmann theory. Our results reveal a clear distinction between late-time (near-equilibrium) and short-time (far-from-equilibrium) relaxation rates, the ratio of which contains information on the charge valency and ad- or desorption mechanism of the charging process. Similarly, we find that single-ion reactions can be distinguished from two-ion reactions, as the latter show an inflection point during equilibration. Interestingly, such inflection points are characteristic of autocatalytic reactions, and we conclude that the Coulombic ion-surface interaction is an autocatalytic feedback mechanism.

DOI: [10.1103/PhysRevLett.130.058001](https://doi.org/10.1103/PhysRevLett.130.058001)

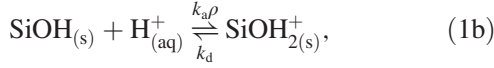
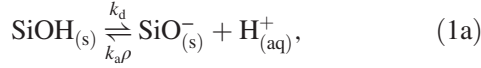
Charged solid-liquid interfaces play a central role in a wide variety of industries such as food and coating production [1–3], mining [4–6], medicine [7–9], soil remediation [10–12], and even carbon capture [13]. With the advent of nanoscale fluidics, one expects that charged surfaces will become ever more important [14,15]. In water and other polar solvents, chemical reactions are a common mechanism by which surfaces obtain their charge. For ionic solids, the de- or adsorption of a dissolved ionic compound is often preferred over the sorption of its own counterion [16–18]; for covalent solids such as polymers and metal oxides, the acidic nature of surface groups ensures that the surface (de)protonates in polar solvents and hence becomes charged [17–21]. However, for many processes of industrial and environmental importance, relatively little is known about the surface chemistry [17–19], as the electrolytes in realistic applications contain a large variety of ions that can all undergo multiple reactions [17,18,22]. Due to experimental limitations, the majority of studies investigating surface charging are performed at (quasi)equilibrium conditions [17,18], with the notable exception of pressure-jump experiments [23,24]. Only recently, however, it has been shown that the kinetics of chemical surface reactions can strongly couple to electrokinetic fluid flows, thereby affecting the physical surface properties on macroscopic scales [18,25–29]. Furthermore, with the recent advent of fast and surface-specific nonlinear spectroscopy, the dynamic measurement of surface charge has become feasible [29–34]. In this context, it has been explicitly stated that there is an urgent need for theoretical models to

describe such experiments [35]. Traditionally, sorption kinetics is typically described by (pseudo-)first-order reactions [12,36,37] that exhibit single-exponential relaxation towards equilibrium; the influence of a time-dependent surface charge is usually neglected entirely [35,38,39]. We are aware of one theoretical work [40] and associated review [41] that consider a surface charge that affects the rate constants of ion association, which, however, do not consider the (chemistry-specific) nonlinear dynamics induced by the electrostatic feedback as we do here.

In this Letter, we present a theory for the charging dynamics of solid surfaces. We include the Coulombic ion-surface interactions and reveal an intricate dependence on the reaction mechanism and the valency of the reactive ions already present in a mean-field description. The Coulomb interactions not only affect the time constant of the late-time exponential decay of the surface charge towards equilibrium after an ion concentration (or pH) shock, but they also induce strongly nonlinear dynamics at early times far from equilibrium. Combined with the present-day capability to experimentally measure the time-dependent surface charge density, our theory forms a first step to unveil the surface chemistry of technologically important but ill-understood materials [18,35], such as silica [22,42] and graphene [43], and of processes such as the cleanup of radioactive and heavy metals [10,16,44,45].

Surfaces—for instance, silica—in water commonly charge either by the desorption of ionic species from neutral surface groups or by the adsorption of ionic species onto neutral surfaces. While the exact charging mechanism

of the silica-water interface is complex, there is support for charging by desorption of protons at high pH and adsorption of protons at low pH [22,42,46,47]:



where $\text{SiOH}_{(s)}$ is a neutral silanol group that is covalently bound to the (solid) glass, and where $\text{SiO}^-_{(s)}$ and $\text{SiOH}^+_{2(s)}$ denote a silanol group with a proton desorbed or adsorbed in Eqs. (1a) and (1b), respectively. Here, ρ denotes the proton density at the solid surface, and the dissociation and association rates k_d and k_a will be discussed below for the charging kinetics of a single desorptive and a single adsorptive reaction, not only for monovalent reactive ions as in Eqs. (1a) and (1b), but for general valency z . While adsorption isotherms of real materials can rarely be described by just a single charging reaction [16,47], we show in the Supplemental Material [48] that charging by multiple reactions can actually be well approximated by the single-reaction kinetics presented in this Letter for a wide range of experimental conditions.

We consider a macroscopic surface with a density Γ of identical surface groups. A group can only be in either a neutral or a charged state. The charging is assumed to take place either by desorption (labeled by $-$) of a cation of charge ze , or by adsorption (labeled by $+$) of a cation of charge ze , with $z \geq 0$ and e the proton charge. The surface densities of charged and neutral groups are denoted by $\sigma_{\pm} > 0$ and $\Gamma - \sigma_{\pm} > 0$, respectively, and the surface charge density is given by $\pm ze\sigma_{\pm}$. Note that the charging dynamics is invariant under the sign of the reacting ions, and without loss of generality we can restrict attention to reactive cations of (strictly positive) valency z . Assuming the chargeable surface sites to be independent, we can describe the reaction kinetics in terms of the time-dependent surface density $\sigma_{\pm}(t) > 0$, which satisfies Langmuir kinetics described by [51,52]

$$\partial_t \sigma_- = k_d(\Gamma - \sigma_-) - k_a \sigma_- \rho(\sigma_-) \quad (2a)$$

for desorptive charging reaction (1a), and

$$\partial_t \sigma_+ = k_a(\Gamma - \sigma_+) \rho(\sigma_+) - k_d \sigma_+ \quad (2b)$$

for adsorptive charging reaction (1b). Here, k_d and k_a are the rate constants of the dissociation and association of the reactive ion, and $\rho(\sigma_{\pm})$ is the volumetric concentration of reactive ions at the surface, which is defined at the position where the rate-limiting step for the reaction occurs [52,53]. We consider this surface to be impermeable to nonreacting ions and therefore do not account for any Stern layer other

than the charged surface groups [27]. The equilibrium surface charge follows from $\partial_t \sigma_{\pm} = 0$ and is given by $\sigma_{\pm,eq} = \Gamma(1 + (k_a \rho_{eq}/k_d)^{\mp 1})^{-1}$, which reduces to an explicit ‘‘Langmuir isotherm’’ in the case that the equilibrium concentration of the reactive ions $\rho_{eq} \equiv \rho(\sigma_{\pm,eq})$ is a constant independent of $\sigma_{\pm,eq}$. In general, however, this Langmuir isotherm is a self-consistency equation for $\sigma_{\pm,eq}$ that requires an additional ‘‘closure’’ relation $\rho(\sigma_{\pm})$ for an explicit equilibrium solution $\sigma_{\pm,eq}$. Without (Coulombic) interactions between the surface and ions, the local concentration $\rho(\sigma_{\pm})$ of reactive species in the vicinity of the surface would be equal to the bulk concentration ρ_b of the reactive ions far from the surface (which is independent of σ_{\pm} , and hence also independent from the reaction mechanism), such that Eqs. (2a) and (2b) would be linear differential equations whose solution can be written as $s_{\pm}(t) = 1 + (s_{\pm}(0) - 1) \exp[-(k_d + k_a \rho_b)t]$ with the dimensionless charge $s_{\pm} = \sigma_{\pm}/\sigma_{\pm,eq}$ such that $s_{\pm,eq} = 1$; here, $s_{\pm}(0) - 1$ is the integration constant and denotes the relative deviation from equilibrium at the initial time $t = 0$. Note that the condition that $0 \leq \sigma_{\pm}(t) \leq \Gamma$ implies that $0 < s_{\pm}(0) < \Gamma/\sigma_{\pm,eq}$, where the lower bound corresponds to an initially neutral surface, whereas the upper bound can be as large as $\mathcal{O}(10\text{--}100)$, since typical equilibrium conditions have a charge occupancy of only a few percent of the total number of chargeable groups [54]. Thus, from measurements of $\sigma_{\pm}(t)$ at various concentrations of reactive (dissolved) species, both k_d and k_a could in this non-interacting case be determined.

However, as the charged surface attracts or repels reactive ions, Eqs. (2a) and (2b) are complicated by a nontrivial relation $\rho(\sigma_{\pm})$, which causes a charge-dependent decay rate and introduces deviations from purely single-exponential relaxation of $\sigma_{\pm}(t)$. In fact, an explicit function $\rho(\sigma_{\pm})$ is needed to investigate and solve the dynamics, which we will develop here. We consider the planar and homogeneous chargeable solid surface discussed above in contact with a bulk solvent with permittivity ϵ and temperature T with a three-component $1:1:z$ electrolyte of bulk concentrations $\rho_s:(\rho_s - z\rho_b):\rho_b$. For convenience, we assume trace amounts of reactive ions and therefore set $\rho_b \ll \rho_s$, where ρ_s is the bulk salt concentration. We also assume the electrolyte volume to be macroscopically large, such that ρ_b and ρ_s do not change due to surface charging. Furthermore, we assume the charging timescale τ_{\pm} , which remains to be derived, to be the slowest timescale of the system. Given that the typical timescale for electric double-layer (EDL) equilibration is around $10^{-9} - 10^{-6}$ s and that the (geometry- and flow-dependent) transport timescale for ions in stirred reactors can be as short as 10^{-4} s [55], we find a large window $\tau_{\pm} \gg 10^{-4}$ s for reactions to be well described by our (reaction-limited) theory [56]: for example, phosphate desorption shows characteristic reaction timescales of hours [57], and adsorption of transition

metals can occur on millisecond timescales [23,24]. The slow-reaction assumption allows us to describe the EDL within an equilibrium theory, for which we take the Gouy-Chapman solution of Poisson-Boltzmann (PB) theory for simplicity [20,58]. Although PB theory is based on a mean-field assumption for a system of point ions, it is known that for all but the highest salt concentrations, this theory is quite accurate for 1:1 and even 1:2 aqueous electrolytes [59], and we expect a similar accuracy for 1:1: z electrolytes in the limit $\rho_b \ll \rho_s$ of our interest. Within these assumptions, the concentration of reactive ions at the surface is determined by a Boltzmann distribution $\rho(\sigma_{\pm}) = \rho_b \exp[-z\phi(\sigma_{\pm})]$, where $k_B T \phi(\sigma_{\pm})/e$ is the electric potential at the surface with a surface charge $\pm z e \sigma_{\pm}$, with k_B being the Boltzmann constant. For desorptive charging, the surface and ions have opposite charges and hence $z\phi(\sigma_{-}) < 0$, while for adsorptive charging, the ions and surface have the same sign, yielding $z\phi(\sigma_{+}) > 0$. With this observation, the Gouy-Chapman solution for a 1:1 electrolyte, which is relevant here as $\rho_s \gg \rho_b$, gives $\phi(\sigma_{\pm}) = \pm 2 \sinh^{-1}(z\sigma_{\pm}/\sigma^*)$ [20,58], where $\sigma^* = (2\pi\lambda_B\lambda_D)^{-1}$, with $\lambda_B = e^2(4\pi\epsilon k_B T)^{-1}$ being the Bjerrum length of the solvent and $\lambda_D = (8\pi\lambda_B\rho_s)^{-\frac{1}{2}}$ the Debye screening length. Substituting the Gouy-Chapman potential in the Boltzmann factor yields

$$\begin{aligned} \rho(\sigma_{\pm}) &= \rho_b \exp[-z\phi(\sigma_{\pm})] \\ &= \rho_b \left(\frac{z\sigma_{\pm}}{\sigma^*} + \sqrt{1 + \left(\frac{z\sigma_{\pm}}{\sigma^*}\right)^2} \right)^{\mp 2z}, \end{aligned} \quad (3)$$

where the exponent is positive for desorptive charging and negative for adsorptive charging. Because Eq. (3) is reaction-mechanism dependent, explicit information on the charging mechanism can be deduced from the reaction kinetics as described by combining Eq. (3) with Eqs. (2a) and (2b).

In order to investigate the influence of the Coulombic ion-surface interactions on the charging dynamics, we numerically solve $\sigma_{-}(t)$ from the kinetic Langmuir-Gouy-Chapman Eqs. (2a) and (3). The symbols in Fig. 1(a) present the resulting relative deviations from equilibrium, $s_{-}(t) - 1$, for a desorptive reaction in the experimentally common case of low equilibrium saturation $\sigma_{-,eq} \ll \Gamma$, both for $s_{-}(t=0) = 2$ and 0.01, corresponding to a surface with double the charge compared to equilibrium and an initially almost uncharged surface, respectively, for equilibrium surface potentials of 50 mV ($|\phi_{eq}| = 2$, circles) and 100 mV ($|\phi_{eq}| = 4$, crosses), and for valencies $z = 0, 1, 2, 3$ indicated by the different colors. Figure 1(a) shows that a desorptive surface that is overcharged ($s_{-} > 1$) decays to equilibrium faster than one that is undercharged ($s_{-} < 1$), and the more so for larger valencies z . Interestingly, the sorption of uncharged species ($z = 0$, black symbols) reveals perfect symmetry between

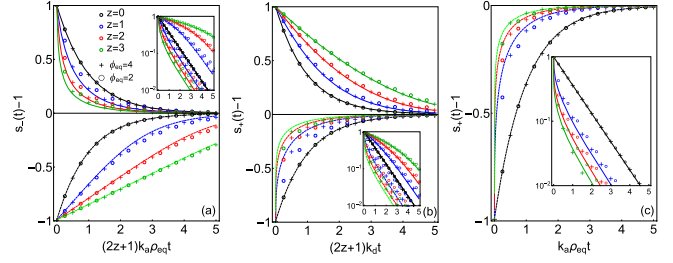


FIG. 1. Time-dependent relative deviations $s_{\pm}(t) - 1$ from the equilibrium charge density as follows from the kinetic Langmuir-Gouy-Chapman equations (2a) and (3) in (a), and Eqs. (2b) and (3) in (b) and (c), for equilibrium zeta potentials $(k_B T/e)|\phi_{eq}|$ equal to 50 mV (crosses) and 100 mV (circles) for valencies $z = 0, 1, 2, 3$ (colors), in (a) $s_{-}(t)$ for desorptive reactions when $\sigma_{-,eq} \ll \Gamma$, in (b) $s_{+}(t)$ for adsorptive reactions when $\sigma_{+,eq} \ll \Gamma$, and in (c) $s_{+}(t)$ for adsorptive reactions when $\sigma_{+,eq} \simeq \Gamma$. Insets denote semilogarithmic representations of $|s_{\pm}(t) - 1|$. The case $\sigma_{-,eq} \simeq \Gamma$ (not shown) is trivial, with single-exponential decay for all z .

the two cases, as expected for first-order kinetics, which is also manifest in the semilogarithmic representation of $|s_{-}(t) - 1|$ in the inset of Fig. 1(a) that shows a data collapse and a single-exponential decay for $z = 0$. For $z \geq 1$, the inset reveals a nonexponential time dependence with an initially slower decay for undercharged surfaces and an initially faster decay for overcharged surfaces, the difference becoming more pronounced for higher valencies. Figure 1(b) shows the deviation $s_{+}(t) - 1$ from numerical solutions of Eqs. (2b) and (3) for an adsorptive charging reaction and the same low equilibrium surface density $\sigma_{+,eq} \ll \Gamma$, and the same surface potentials and valencies as in Fig. 1(a). Interestingly, for this reaction, the relaxation of an initially undercharged surface to equilibrium is faster, rather than slower, as we found for desorptive undercharged surfaces in Fig. 1(a). Hence, the two mechanisms can be distinguished by inspecting a single time-trace of the surface charge. We do not plot the dynamics of a desorptive surface that is saturated in equilibrium $\sigma_{-,eq} \simeq \Gamma$ (in which case $k_d \gg k_a\rho_{eq}$), as the equilibration (dissociation) rate for such a surface $\partial_t s \simeq -k_d(s - 1)$ is linear, and equilibration occurs through trivial single-exponential decay. The lack of nonlinearity for such a surface stems from the fact that the dissociation process is unaffected by the electrostatic surface-ion interaction. However, as can be seen in Fig. 1(c), the dynamics of an adsorptively charged surface with a saturated charge density $\sigma_{+,eq} \simeq \Gamma$ is markedly nonlinear. As was the case in Fig. 1(b), we see that an undercharged surface equilibrates faster than a single exponential. Clearly, these rather distinctive features of the time-dependent surface charge contain explicit information on not only the reaction mechanism but also the valency of reacting ions. Interestingly, such deviations from single-exponential decay have historically been observed in

pressure-jump experiments [23,24]. In the Supplemental Material [48], we show that these experiments are well described by our theory, alleviating the need of introducing multiple reactions to describe such experiments.

In Figs. 1(a) and 1(b), the dimensionless time on the horizontal axes contains a factor $(2z + 1)$, which as we will show now, is convenient, as it leads to a data collapse in the asymptotic nonlinear screening regime $|\phi_{\text{eq}}| \gg 1$, where $s_{\pm}(t)$ only depends on the valency, the reaction mechanism, and the initial charge state. To see why the near-equilibrium decay rate includes a factor $(2z + 1)$ in Figs. 1(a) and 1(b), but not 1(c), we simplify the Langmuir-Gouy-Chapman equations (2a), (2b), and (3) in the important and common case of large equilibrium surface potentials, where $z\sigma/\sigma^* > 1$ —say, beyond 50 mV, where $|\phi_{\text{eq}}| \geq 2$. In this limit, Eqs. (2a) and (2b) can be rewritten as a single polynomial (Chini [60]) differential equation:

$$-\partial_t s_{\pm} = k_a \rho_{\text{eq}} (s_{\pm}^{1 \mp 2z} - s_{\pm}^{-z \mp z}) + k_d (s_{\pm} - s_{\pm}^{-z \mp z}), \quad (4)$$

for which a closed form solution can be obtained by the separation of variables only for an adsorptively charged surface with $k_d \gg k_a \rho_{\text{eq}}$, in which case $s_{\pm}^{2z+1}(t) = 1 + (s_{\pm}^{2z+1}(0) - 1) \exp[-(2z + 1)k_d t]$. Near equilibrium, $s_{\pm} \simeq 1$, Eq. (4) simplifies to the linear differential equation $\partial_t s_{\pm} \simeq -(s_{\pm} - 1)/\tau_{\pm}$ with the near-equilibrium decay rate for desorptive and adsorptive charging given, respectively, by

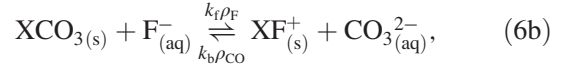
$$\tau_{-}^{-1} = (2z + 1)k_a \rho_{\text{eq}} + k_d, \quad (5a)$$

$$\tau_{+}^{-1} = (2z + 1)k_d + k_a \rho_{\text{eq}}. \quad (5b)$$

As announced, this timescale τ_{\pm} shows that electrostatic attraction can alter the linear, near-equilibrium decay rate by a factor $(2z + 1)$ for $z \geq 1$ compared to the neutral case ($z = 0$) in the experimentally common regime $(k_a \rho_{\text{eq}}/k_d)^{\mp 1} \gg 1$, where $\sigma_{\pm, \text{eq}} \ll \Gamma$. As for the majority of surfaces, the equilibrium charge is much lower than saturation, $\sigma_{\text{eq}} \ll \Gamma$ [54], so we expect the correction by a factor $(2z + 1)$ to be common, and we note in passing that the only other work focusing on the influence of Coulombic ion-surface interactions on kinetics [40,41] does not mention this factor. As already observed in Fig. 1, our simple Eq. (4) shows that far from equilibrium, the dynamics becomes nonlinear, and importantly, the \pm sign of the reaction mechanism breaks the near-equilibrium symmetry of dynamics with regard to a charge excess or a charge deficit. As can be seen from Eq. (3), desorptively charged surfaces which are overcharged, $s_{-} > 1$, will initially attract an excess of reactive ions to the surface, thereby having an increased reaction rate compared to uncharged equilibration. Hence, the equilibration for large overcharging is faster than expected from uncharged Langmuir kinetics. Conversely, an initially

undercharged surface, $s_{-} < 1$, will have a shortage of reactive ions, and thus equilibration will be slower. For adsorptively charged surfaces, equilibration will be nonlinear regardless of $\sigma_{\text{eq}}/\Gamma$, and here undercharging leads to a shortage of reactive ions compared to equilibrium, and hence faster equilibration, as can be seen in Fig. 1(b). The rate changing during equilibration is reminiscent of autocatalytic reactions where the equilibration rate changes because a catalyst speeding up the reaction is produced simultaneously with a reaction product [61–63], and in the Supplemental Material [48] we demonstrate the similarity between Eq. (4) and autocatalytic kinetics. A characteristic feature of such autocatalytic reactions is an increasing decay rate up to a maximum and a corresponding inflection point in the time-dependent decay.

Interestingly, for so-called ion displacement reactions in which ions are involved in both the forward- and the backreaction, inflection points are easily realizable, as there are now two ions attracted or repelled from the charged surface such that the Coulombic feedback is strengthened: inflection points are hence a smoking gun that multiple ions are involved in a charging reaction. An example of a two-ion reaction where all reacting ions are repelled from the charged surface is the calcium charging of silica [42] of Eq. (6a), while an example of a reaction where all the reacting ions are attracted to the charged surface is the fluoride charging of the biomineral carbonato-apatite [64] of Eq. (6b):



where $X = \text{Ca}_{10}(\text{PO}_4)_6$, k_f is the forward (charging) reaction rate, k_b is the backward (discharging) rate, and ρ_i is the concentration of ion species i at the charged surface. In the Supplemental Material [48], we derive under the same Gouy-Chapman and large surface potential conditions of the main text that the charge equilibrations for Eqs. (6a) and (6b) are respectively described by

$$-\partial_t s = k_f \rho_{\text{Ca}, \text{eq}} (s^{-3} - s^{-4}) + k_b \rho_{\text{H}, \text{eq}} (s^{-1} - s^{-4}), \quad (7a)$$

$$-\partial_t s = k_f \rho_{\text{F}, \text{eq}} (s^3 - s^2) + k_b \rho_{\text{CO}, \text{eq}} (s^5 - s^2), \quad (7b)$$

with the resulting near-equilibrium decay constant $\tau = k_f \rho_{i, \text{eq}} + 3k_b \rho_{j, \text{eq}}$ for both reactions. Comparing Eqs. (7a) and (7b) to Eq. (4), we see that now the time evolution is given by the difference of two polynomials of (nonzero) unequal degree, ensuring that there is always a maximum in the decay rate and hence an inflection point. We find that reactions of the form in Eq. (6b) have two physically realizable inflection points located at $s = 2/3$ (if $\sigma_{\text{eq}} \simeq \Gamma$)

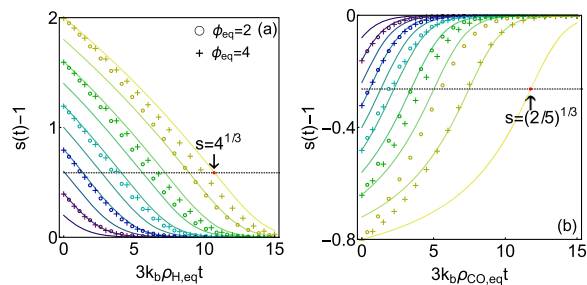


FIG. 2. Time dependence of the relative deviation from the equilibrium charge density $s(t) - 1$ for the autocatalytic ion displacement reaction [Eqs. (7a) and (7b)] for ten different initial conditions $s(0)$ in the experimentally common regime $\sigma_{\text{eq}} \ll \Gamma$. Symbols are numerical solutions for the full Langmuir-Gouy-Chapman equation (Supplemental Material [48]) for $\phi_{\text{eq}} = 2$ (open symbols) and $\phi_{\text{eq}} = 4$ (crosses), for five initial conditions. The gray dashed line denotes the inflection point [top $s(t) - 1 \simeq 0.6$, bottom $s(t) - 1 \simeq -0.25$].

and $s = (2/5)^{1/3} \simeq 0.75$ (if $\sigma_{\text{eq}} \ll \Gamma$): the reaction in Eq. (6a) has only one accessible inflection point $s = 4^{1/3} \simeq 1.6$ (if $\sigma_{\text{eq}} \ll \Gamma$), while its second inflection point $s = 4/3$ is inaccessible for a saturated surface with $\sigma_{\text{eq}} \simeq \Gamma$.

We plot the dynamics resulting from Eqs. (7a) and (7b) for a variety of starting conditions $s(0)$ in Fig. 2 in the experimentally common limit $\sigma_{\text{eq}} \ll \Gamma$. In Fig. 2(a), excellent agreement between the asymptotic Eq. (7a) and full numerical results can be seen, while in Fig. 2(b) for large undercharging $s(0) < 0.2$, a discrepancy between Eq. (7b) and the full numeric solution is found. However, in general, Eqs. (7a) and (7b) predict the location of the inflection point accurately for a range of common surface potentials $(k_{\text{B}}T/e)|\phi_0| \in [50, 100]$ mV. For ion-displacement reactions of the forms in Eqs. (6a) and (6b) involving ions with higher valencies but monovalent surface charge, the inflection point will lie even closer to equilibrium. Thus, surfaces that are initially undercharged by only $\simeq 25\%$ or overcharged by $\simeq 60\%$ will generally equilibrate along sigmoidal curves, which is a distinguishing feature that cannot be observed for the single-ion reactions in Eqs. (1a) and (1b). Finally, we note that ion-displacement reactions offer a simple explanation for the recently observed sigmoidal equilibration of the surface charge at an aqueous silica interface [63] using only a single charging reaction of the form Eq. (6a) rather than the proposed autocatalytic dissolution cycle involving multiple steps.

To summarize, in this Letter we present a model for the nonlinear dynamics of reaction-limited surface charging, combining Langmuir dynamics with Poisson-Boltzmann theory. The model captures how the screened electrostatic surface-ion interaction affects the reaction rate near and far from equilibrium in terms of a nonlinear differential equation, where the electrostatic interaction is described by only using the charge valency of the reactive ion. The

Coulombic ion-surface interaction leads to a charge-dependent decay rate, which can be used to gain information on the valency of reacting ions, initial charge, and reaction rate. De- and adsorptive reactions can be distinguished by inspecting whether far-from-equilibrium decay is slower or faster than near-equilibrium decay, while an inflection point is characteristic for two-ion reactions. Interestingly, we note that inflection points are a characteristic feature of autocatalytic reactions and that the electrostatic ion-surface interaction can be seen as a catalytic feedback loop. Hence, electrostatics offers a straightforward explanation for the recently measured autocatalytic charging of silica [63].

We thank Ben Werkhoven and Cheng Lian for fruitful discussion, and an anonymous referee for pointing us to the pressure-jump experiments in Refs. [23,24]. This work is part of the D-ITP consortium, a program of the Netherlands Organisation for Scientific Research (NWO) that is funded by the Dutch Ministry of Education, Culture and Science (OCW).

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