Charge inversion by multivalent ions: Dependence on dielectric constant and surface-charge density

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Charge inversion occurs when the effective charge of a surface exposed to solution reverses polarity due to an excess of counterions accumulating in the immediate vicinity of the surface. Using atomic force spectroscopy, we have directly measured the effect on charge inversion of changing the dielectric constant of the solvent and the surface-charge density. Both decreasing the dielectric constant and increasing the bare surface-charge density lower the charge-inversion concentration. These observations are consistent with the theoretical proposal that spatial correlations between ions are the dominant driving mechanism for charge inversion.

I. INTRODUCTION

Screening by mobile ions dominates electrostatic interactions in electrolytes, making it a very important element of polymer physics, nanofluidics, colloid science, and molecular biophysics. In the presence of multivalent ions, counterintuitive phenomena occur such as attraction between like-charged molecules [1] and its converse, repulsion between oppositely charged objects [2]. Similarly, the electrophoretic mobility of charged colloids can reverse sign in the presence of multivalent ions [3,4], a phenomenon known as charge inversion or overcharging. Charge inversion has also been observed and studied using numerical simulations [5,6].

Early observations of the charge inversion of oxides by metal ions were interpreted in terms of specific chemical binding between the multivalent ions and the surface being screened [3,7–9]. This mechanism necessarily relies on the detailed chemical structure of the substances involved, for example the propensity of metal ions to form hydroxides [3,7–9]. Theory, however, suggests that such specific interactions are not necessary for charge inversion to take place [10]. In particular, it has been argued that spatial correlations, ignored in conventional mean-field descriptions of screening on which much of our intuition is based, are highly relevant for multivalent ions and naturally lead to charge inversion. We indeed recently showed [2] that, for a variety of ions, charge inversion is an equilibrium effect that depends very strongly on the valence Z of the ions but can be largely insensitive to their chemical properties, in agreement with these theoretical predictions.

Here we extend these measurements by exploring the dependence of charge inversion on the dielectric constant of the medium and the bare surface-charge density $\sigma_{\text{bare}}$. We compare the results with the predictions from both specific binding and ion-correlation theories.

II. THEORETICAL BACKGROUND

Charge inversion occurs when the concentration of multivalent ions in the bulk solution, $c$, exceeds the so-called charge-inversion concentration $c_0$. We are particularly interested in probing $c_0$ for two related reasons. First, $c_0$ can be determined experimentally without recourse to any particular model. Second, it is a quantity that is particularly amenable to theoretical treatment: since the surface is neutralized at $c = c_0$, fewer assumptions are necessary regarding the structure of the double layer. In this section we first summarize the derivation of a simple, mean-field expression for $c_0$ in terms of specific binding of multivalent ions to the surface, then indicate how this expression is modified by spatial correlations between multivalent ions at the surface.

Consider a surface with bare charge density $\sigma_{\text{bare}}$ in equilibrium with an electrolyte. For large $\sigma_{\text{bare}}$, the double layer is conventionally divided into two regions: the diffuse layer, in which the Poisson-Boltzmann (PB) equation holds, and, close to the surface, the so-called Stern layer. In our simple model, the latter contains a two-dimensional layer of ions (predominantly multivalent in our case) located a distance $d_s$ away from the surface containing a charge density $\sigma_{\text{Stern}}$. The parameter $d_s$ represents the finite size of the ions. For simplicity the charge density is commonly taken to be zero in the range $0 < x < d_s$, where $x$ is the distance from the surface. It is further assumed that multivalent ions are held in the Stern layer not only by electrostatic interaction with the charged surface, but also by a chemical interaction. Specifically, it is assumed that local interactions between each ion and the surface and/or the solvent contribute a change in free energy $\Delta \mu^{0\ast}$ upon taking one multivalent from the bulk to the Stern layer. The parameter $\Delta \mu^{0\ast}$ includes any complex formation between the ion and the surface. It can in general be expected to depend on specific properties of the system such as chemical composition, surface structure, and lipophilicity of both the ions and the surface. $\Delta \mu^{0\ast}$ cannot be predicted reliably at this time: in comparing to data it is typically treated as an empirical fitting parameter.

In equilibrium, the electrochemical potential of the multivalent ions in the bulk is equal to that of multivalent ions in the Stern layer [11]. These electrochemical potentials are, respectively, $\mu_0 = \mu_0^{\ast} + kT \ln(c/c_{\text{max}}) + Ze\phi(\infty)$ and $\mu_s = \mu_s^{\ast} + kT \ln(c_s/c_{s,\text{max}}) + Ze\phi(d_s)$. Here the activity coefficients have been set to unity [11]. $\mu_0^{\ast}$ and $\mu_s^{\ast}$ are constant parameters such that $\mu_0^{\ast} - \mu_s^{\ast} = \Delta \mu^{0\ast}$. $c$ and $c_{\text{max}}$ are, respectively, the concentration and maximum concentration of multivalent ions in the bulk, $c_s$ and $c_{s,\text{max}}$ are, respectively, the two-

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the potential in the bulk $\psi(\infty)$ was taken as zero.

In the region $0 < x < d_s$, the potential $\psi$ varies linearly with $x$ to the value $\psi(d_s)$. For $x > d_s$, $\psi(x)$ drops to the bulk value according to the PB equation. Figure 1(a) sketches the potential $\psi(x)$ for the cases when the Stern layer almost compensates the surface charge ($c < c_0$, $|\sigma_{\text{Stern}}| < |\sigma_{\text{bare}}|$), fully compensates the surface charge ($c = c_0$, $|\sigma_{\text{Stern}}| = |\sigma_{\text{bare}}|$), and overcompensates the surface charge ($c > c_0$, $|\sigma_{\text{Stern}}| > |\sigma_{\text{bare}}|$).

At $c = c_0$ the bare surface charge is entirely compensated by the charge in the Stern layer, thus $c_s = |\sigma_{\text{bare}}|/2r_e$ and $\psi(d_s) = 0$. Further taking on geometrical grounds that $c_{\text{s,max}}/c_{\text{max}} = 2r$, where $r$ is the radius of an ion, Eq. (1) then yields for the charge-inversion concentration

$$c_0 = \frac{\sigma_{\text{bare}}}{2r_e Z_e} \exp\left(\frac{\Delta \mu^0}{kT}\right).$$

For specific binding to account for charge inversion, $\Delta \mu^0$ must be negative and several times $kT$ in magnitude.

Real surfaces become charged in an electrolyte by the dissociation of charged groups (ions) from the surface or association of charged groups to the surface [12]. Such chemical equilibrium between surface sites and charge-determining ions renders $\sigma_{\text{bare}}$ dependent on the concentration of charge-determining ions at the surface, and thus on the bulk concentration of all ions in the solution including the multivalent ions. This so-called charge regulation does not affect the condition for charge inversion given by Eq. (2), however, and only enters Eq. (2) implicitly via $\sigma_{\text{bare}}$. In situations where charge regulation plays a significant role, the value of $\sigma_{\text{bare}}$ must be obtained self-consistently for the condition $\psi(d_s) = 0$ and $c = c_0$. Since experimentally $\sigma_{\text{bare}}(c_0)$ is difficult to determine independently, we will treat it as an unknown parameter.

So far we have discussed the influence of regulation of the bare surface charge due to equilibrium with a bulk reservoir. Additional regulation effects can occur when two surfaces are brought into such proximity to each other that they influence each other’s double layers. This effect can even result in a reversal of the force of interaction as a function of the distance between the surfaces [13–15]. Since our experiments mostly focus on long-range interactions (distance greater than $2\lambda$, where $\lambda$ is the Debye length) and that such regulation effects become important at shorter range, we do not consider these effects further here.

Several authors have attempted descriptions beyond the mean-field one outlined above and incorporated the role of spatial correlations between multivalent ions in the Stern layer. Here we concentrate on the formalism introduced by Shklovskii [16], which hinges on the theoretical observation that multivalent ions must form a strongly correlated ionic liquid in the Stern layer of surfaces with high $\sigma_{\text{bare}}$. This formalism leads to simple analytical expressions for the charge-inversion concentration $c_0$. The development parallels that given above, with the additional refinement that $\Delta \mu^0$ is replaced by $\Delta \mu^1 + \mu_c$. Here $\Delta \mu^1$ represents hydration and specific binding effects while $\mu_c$ accounts for spatial interactions between multivalent ions in the Stern layer. The predicted value for the charge-inversion concentration is then

$$c_0 = \frac{\sigma_{\text{bare}}}{2r_e Z_e} \exp\left(\frac{\mu_c}{kT}\right) \exp\left(\frac{\Delta \mu^0}{kT}\right),$$

with $\mu_c$ given by [16,17]

$$\mu_c = -kT(1.65\Gamma - 2.611\Gamma^{1/4} + 0.26 \ln \Gamma + 1.95),$$

and the interaction parameter $\Gamma$ by

$$\Gamma = \frac{1}{4kT\epsilon_0} \sqrt{\frac{e^2 Z_e^2 \sigma_{\text{bare}}}{\pi}} ,$$

where $\epsilon_0$ is the permittivity of free space. This theory holds for $\Gamma > 1$ [16,18], which is typically fulfilled for $Z \geq 3$. For example, when $Z = 3$, $\sigma_{\text{bare}} = 0.5$ e/nm$^2$, and $\epsilon = 80$, the value of $\Gamma$ is 4.6. Calculated values of $\Gamma$ from our experiments are in the range $3 \leq \Gamma \leq 8$. For $\Gamma > 1$, $\mu_c$ is approximately equal to the first term in Eq. (4), yielding $\mu_c \propto -\sqrt{\sigma_{\text{bare}}^2}/\epsilon$. Thus while we use the full expression for $\mu_c$ in our calculations, the approximation is expected to correctly predict the qualitative trends. For monovalent salt ($Z = 1$) at room temperature, $\Gamma \approx 1$ and correlation effects do not play a significant role [16,18,19].

Equation (3) predicts that charge inversion can occur even in the absence of specific adsorption ($\Delta \mu^0 \neq 0$). Correlations are then solely responsible for charge inversion. The depen-
III. EXPERIMENTAL METHODS

We have determined the charge-inversion concentration through a direct measurement of the electrostatic interaction between two oppositely charged surfaces, as described previously [2]. In short, we used a Digital Instrument NanoScope IV Atomic Force Microscope (AFM) to measure the force $F$ between the surfaces versus their separation $d$ in different concentrations $c$ of an asymmetric $Z:1$ electrolyte. The sign of the force far from contact unambiguously yields the effective polarity of the surface being screened by the multivalent counterion.

The negatively charged surface consisted of a silica bead glued to an AFM cantilever. The AFM cantilever was heated with a soldering iron. Using a micromanipulator, a small amount of epoxy resin (EPI-REZ 3522-W-60) was deposited on the hot tip of the cantilever. Next, a 10 $\mu$m silica sphere (G. Kisker Gbr) was deposited from a glass microscope slide on the tip of the cantilever. Upon cooling, the resin solidified and the bead remained attached to the end of the tip [20]. In contact with water silica gets charged by the dissociation of silanol groups, $(Si)OH \rightleftharpoons (Si)O^– + H^+$, where (Si) is a silicon atom at the surface.

The positively charged amine-terminated surface was prepared from a silicon dioxide surface. A silicon substrate with 300–500 nm thermally grown oxide was first immersed in a 3:1 mixture of sulfuric acid and hydrogen peroxide for 15 min and rinsed with deionized Milli-Q filtered water (mq water). In a glove box containing a nitrogen environment, it was then immersed in a 0.1% solution of 1-trichlorosilyl-11-cyanoundecane $[NC(CH_2)_{11}SiCl_3]$ (Gelest) in toluene for 30 min and rinsed in clean toluene. The trichlorosilane group of the molecule binds covalently to the surface. The substrate was then sonicated in toluene, chloroform, and again toluene, each for 5 min in an acid hood. Back in the glove box, it was immersed in a 20% solution of Red Al (Sigma-Aldrich) in toluene for 5 h and afterwards rinsed in clean toluene. The Red Al reduces the cyano group to an amino group. Finally, the substrate was sonicated in, respectively, toluene, acetone, mq water, nitric acid ($pH$ 2), and mq water each for 5 min and blown dry. The substrate was kept under nitrogen atmosphere until used. In contact with water the amino group can take up a proton, $(Si)–R–NH_2 + H^+ \rightleftharpoons (Si)–R–NH_3^+.$

The AFM cantilever (ThermoMicroscope Microlever) had a nominal force constant of about 0.03 N/m, as specified by the manufacturer. Absolute values of force shown here are based on this value.

We present results using five different multivalent ions. The same molecule in two different charge states, iron(II) hexacyanide $[Fe(CN)_{6}]^{3–}$ ($r \approx 443$ pm) and iron(III) hexacyanide $[Fe(CN)_{6}]^{4–}$ ($r \approx 437$ pm) [21–23], both with $K^+$ counterions, was used to investigate charge inversion on the positively charged amine-terminated surface. Three positive trivalent ions with a different chemical composition were used to investigate charge inversion on the negatively charged silica bead. All three have $Cl^–$ counterions. Lanthana-

IV. FORCE-DISTANCE CURVES

Figure 2 shows the measured force $F$ versus the distance $d$ between a silica bead and an amine-terminated surface. Three curves are shown that correspond to three different electrolytes. The observed $F(d)$ curves are dramatically different for the three cases.

The curve represented by squares (bottom curve) was obtained in a solution containing 0.5 mM monovalent salt. At bead-surface separations less than about 75 nm, an attractive (negative) force was observed that increased in magnitude with decreasing separation. Below about 35 nm separation, the attractive force gradient exceeded the spring constant of...
the cantilever and the bead snapped to the surface.

The curve represented by circles (top curve) was obtained in a solution containing 50 μM −4: +1 salt in addition to the monovalent salt. A repulsive (positive) force was clearly observed below about 55 nm separation, which we interpret as indicating that charge inversion of the positive surface has occurred. The force increased with decreasing distance until \( d = 13 \) nm. For \( d \) in the range 8–13 nm, the force instead decreased with decreasing distance. Below 8 nm snap-in occurred.

The curve represented by triangles (middle curve) was obtained in a solution containing a 1 M monovalent salt. The Debye screening length \( \lambda \) of this solution is \( \approx 0.3 \) nm, and hence electrostatic interactions are expected to play no role except at extremely small separations. The observed force remained zero until the distance \( d \) was only about 5 nm. Below this distance a weak attractive force was observed which we attribute to van der Waals forces. The data show that van der Waals forces are negligible for \( d > 10 \) nm.

In order to quantitatively describe the \( F(d) \) curves, we distinguish between two main regimes depending on whether the separation \( d \) is greater or smaller than about twice the Debye length \( \lambda \) of the solution.

In the regime \( d \geq 2\lambda \), the force \( F \) between the silica bead and amine-terminated surface is expected from the Poisson-Boltzmann equation to decay exponentially with \( d \):

\[
F(d) = F_0 \exp(-d/\lambda), \quad d \geq 2\lambda.
\]  

The parameter \( F_0 \) is not the real force at zero separation, but rather the value of the force when the functional form valid far from the surface is extrapolated to the surface. Theoretically \( F_0 \approx \sigma_0^* \sigma_0^* \), where \( \sigma_0^* \) and \( \sigma_r^* \) are the so-called renormalized surface-charge densities of the silica bead and of the amine-terminated surface, respectively. \( \sigma_0^* \) and \( \sigma_r^* \) are related to the net surface-charge densities of the bead and the amine-terminated surface, \( \sigma_0 \) and \( \sigma_r \), which include both the bare surface charge and the charge in the Stern layer. At low net surface-charge density \( \sigma_{b,0} < \sigma_{\text{max}} = 4kT\epsilon\epsilon_0/e\lambda \), the renormalized charge densities are simply equal to the net charge densities: \( \sigma_{b,0}^* = \sigma_{b,0} \). At higher net charge densities, \( \sigma_{b,0}^* \) saturates at \( \sigma_{\text{max}}^* \).

Because we use oppositely charged surfaces and asymmetric Z:1 electrolytes and correlation effects are only relevant for \( Z > 1 \), charge inversion is only expected to occur at one of the surfaces. The other surface, screened predominantly by monoionic salts, can thus be thought of as a constant probe. Near charge inversion, \( F_0 \) is thus approximately proportional to the net surface-charge density of the surface being screened by multivalent ions, \( \sigma_0 \) or \( \sigma_r \), and the sign of the force unambiguously yields the polarity of this net surface charge. Note that, strictly speaking, the value of \( \sigma_0^* = \sigma_{\text{max}}^* \) for the probe is not constant since it depends linearly on \( \lambda^{-1} \) and more subtly on the valence of the ions [26]. This introduces a small systematic error in the fitted value of \( \epsilon_0 \), but does not affect the measured sign of the force.

The solid lines in Fig. 2 show fits of the data to Eq. (6) in which \( F_0 \) and \( \lambda \) are used as fitting parameters. The fitted values of \( \lambda \) are 13.9 and 12.6 nm for the measurements in the monovalent electrolyte and in the electrolyte containing multivalent ions, respectively. The calculated values of \( \lambda \) for these electrolytes are 13.6 and 9.6 nm, respectively. Equation (6) gives less good quantitative agreement with the data obtained in the charge-inversion regime. It also fails to capture the decrease in \( F \) with decreasing \( d \) at short range in this case. This is not unreasonable since Eq. (6) becomes increasingly inaccurate with decreasing \( d \). The leading correction [14] yields

\[
F = F_0 \exp(-d/\lambda) + F_1 \exp(-2d/\lambda),
\]

which reduces to Eq. (6) at large enough separations. Here \( |F_1| \approx \sigma_r^* \). Near charge inversion of one of the two surfaces, the \( F_1 \) term in Eq. (7) becomes much more prevalent. This is because \( \sigma_1^* \) vanishes at \( c_0 \) for the surface being charge inverted while \( \sigma_r^* \) of the other surface remains \( \approx \sigma_{\text{max}}^* \), leading to a vanishing \( F_0 \) and a largely unaffected \( F_1 \). Equation (6) can therefore be expected to be less accurate near charge inversion, as observed.

The sign of \( F_1 \) depends on the boundary conditions of the system: surfaces with constant net surface-charge density give positive values of \( F_1 \) (repulsive force), while surfaces at constant potential give negative values of \( F_1 \) (attractive force) [13–15,20]. A surface whose net surface charge is strongly regulated behaves as being at constant potential, and this is also the case that is predicted to apply for the net surface charge in the presence of a strongly correlated Stern layer [14].

The dashed line in Fig. 2 gives a fit of Eq. (7) to the measurement in the presence of multivalent ions, where \( F_0 \), \( F_1 \), and \( \lambda \) are used as fitting parameters. The fitted value of \( F_1 \) is negative, implying that the surface screened by multivalent ions indeed behaves as if held at a constant potential. The fitted value of \( \lambda \) is 11.6 nm, in better agreement with the expected value than the fit to Eq. (6).

In the remainder of this paper we concentrate on the regime where both \( d \geq 2\lambda \) and van der Waals forces are small (\( d > 10 \) nm), where we can reliably fit to Eq. (6). Under these conditions and near charge inversion, \( F_0 \) is approximately proportional to the net surface-charge density of the surface being screened by multivalent ions and the sign of the force unambiguously yields the polarity of this net surface charge.

V. DIPOLE CONSTANT \( \epsilon \)

We have measured the influence of the dielectric constant of the solvent on the charge-inversion concentration by using water-alcohol mixtures as the solvent. These were prepared by mixing solutions of 2 mM KOH and 2 mM HCl (both in water) to the desired pH value, then diluting with MQ water and/or ethanol to obtain mixtures with dielectric constant \( \epsilon = 80 \) (only water), 68 (75% water, 25% ethanol) and 54 (50% water, 50% ethanol). The values of the dielectric constant were obtained by interpolating between tabulated values for water-ethanol mixtures [27].

Figure 3 shows an experiment where the same amine-terminated surface was charge inverted with [Fe(CN)]\(^{3+}\) in electrolytes with different dielectric constants. The same silica bead was used during the entire experiment. After changing the dielectric constant of the solution, a part of the
amino-terminated surface that had not been in contact with the electrolyte during the previous measurement was used. The data clearly show that a lower concentration of multivalent ions is required to cause charge inversion when the dielectric constant is reduced.

We fitted $F(d)$ curves to Eq. (6) in the range $d > 2 \lambda$ and extracted the force $F_0$. Because it is difficult to accurately fit $\lambda$ when the force is very small, the value of $\lambda$ was only fitted for the curve with $c = 0$ and corrected using the standard expression when $c > 0$. Figure 3(a) shows such fits to Eq. (6) as lines through the data.

Figure 3(d) shows $F_0$ versus multivalent ion concentration $c$. Each point represents the average of five separate fits. To facilitate comparison between different curves, the value of $F_0$ was normalized to its value when $c = 0$ for each curve: $F_{N0}(c) = F_0(c)/F_0(0)$. We estimate the charge-inversion concentration $c_0$ by linearly interpolating between the data points immediately above and below $F_{N0} = 0$ on the log-log scale. The resulting values of $c_0$ are 12, 5, and 1 $\mu$M for $\epsilon = 80$, 68, and 54, respectively. Thus lowering the dielectric constant from 80 to 54 causes a decrease of the charge-inversion concentration by a factor $\approx 10$.

At the end of each experiment, $F(d)$ was measured at the same concentration $c$ of multivalent ions as was used at the beginning of the experiment (open circles in Fig. 3). In water, the resulting curve was usually identical to that measured at the beginning of the experiment [see, for example, Fig. 3(a)]. In water-ethanol mixtures, however, the magnitude of the force often decreased after prolonged exposure [Figs. 3(b) and 3(c)]. This was also observed in the absence of multivalent ions, indicating that exposure to ethanol induced a slow decrease of the magnitude of the surface charge. To minimize the influence of this on further analysis, we compare data that were obtained on surfaces exposed to solution for approximately the same duration.

Figure 4 shows similar experiments using the multivalent ions [Fe(CN)$_6$]$^{3-}$ and [Co$_{12}$H$_{30}$N$_8$]$^{3+}$, and 0.5 mM KCl as monovalent salt. When decreasing $\epsilon$ from 80 to 54, $c_0$ decreased by a factor 7 for [Fe(CN)$_6$]$^{3-}$ and 16 for [Co$_{12}$H$_{30}$N$_8$]$^{3+}$.

Figure 5 shows a comparison between the three trivalent positive ions. In each case decreasing $\epsilon$ causes a decrease in $c_0$ irrespective of chemical structure. The values of $c_0$ for the three ions are within a factor of 2 at $\epsilon = 80$ and within a factor of 4 at $\epsilon = 54$. The decrease in $c_0$ when decreasing $\epsilon$ from 80 to 54 is a factor of 23 for [Ru(NH$_3$)$_6$]$^{3+}$, 47 for La$^{3+}$, and 30 for [Co$_{12}$H$_{30}$N$_8$]$^{3+}$ for these particular surfaces. In these measurements HEPES (4-(2-hydroxyethyl)piperazin-1-ethanesulfonic acid) buffer was used as the monovalent salt because of the atypical behavior of La$^{3+}$, namely, the $pH$ of an unbuffered La$^{3+}$ solution decreased from $pH$ 7 to $pH$ 5.5–6.0 upon adding 1 mM La$^{3+}$. At this La$^{3+}$ concentration impurities also sometimes appeared in the solution over time. In addition, recovery of an attractive signal after charge
lead to significant variations in the observed charge ratios. Water in the solutions and the age of the stock solutions can add to the ratio ultimately deposited on the surface. In addition, the preparation of the amine-terminated surfaces is sensitive to the ratio deposited on the surface. Inversely, the preparation of the trivalent ions using the trivalent ions [CoC\(_{12}\)H\(_{30}\)N\(_8\)]\(^{3+}\) (squares), [Ru(NH\(_3\))\(_6\)]\(^{3+}\) (circles), and La\(^{3+}\) (triangles). Electrolytes containing 1 mM HEPES of pH 7.3±0.2 with \(\varepsilon=54\) (open symbols) were used. The values of \(c_0\) for \(\varepsilon=54\) and 54 are 300 and 10 \(\mu\)M for [CoC\(_{12}\)H\(_{30}\)N\(_8\)]\(^{3+}\), 520 and 23 \(\mu\)M for [Ru(NH\(_3\))\(_6\)]\(^{3+}\), and 280 and 6 \(\mu\)M for La\(^{3+}\).

**FIG. 5.** (Color online) Normalized force \(F_{N0}\) versus multivalent ion concentration \(c\) for three experiments in which a silica bead was charged inverted using the trivalent ions [CoC\(_{12}\)H\(_{30}\)N\(_8\)]\(^{3+}\) (squares), [Ru(NH\(_3\))\(_6\)]\(^{3+}\) (circles), and La\(^{3+}\) (triangles). Electrolytes containing 1 mM HEPES of pH 7.3±0.2 with \(\varepsilon=54\) (filled symbols) and \(\varepsilon=80\) (open symbols) were used. The values of \(c_0\) for \(\varepsilon=80\) and 54 are 300 and 10 \(\mu\)M for [CoC\(_{12}\)H\(_{30}\)N\(_8\)]\(^{3+}\), 520 and 23 \(\mu\)M for [Ru(NH\(_3\))\(_6\)]\(^{3+}\), and 280 and 6 \(\mu\)M for La\(^{3+}\).

inversion had occurred in the \(\varepsilon=54\) solvent with La\(^{3+}\) took three times longer than usual. This indicates a reaction involving La\(^{3+}\) in which small quantities of H\(^+\) ions (less than one per 100 La\(^{3+}\) ions) are released [3]. This behavior was never observed with ions other than La\(^{3+}\).

VI. SURFACE-CHARGE DENSITY \(\sigma_{\text{bare}}\)

We have measured the influence of the bare surface-charge density of the amine-terminated surface on the charge-inversion concentration by changing the amount of chargeable sites on the surface. This was achieved using mixtures of 1-trichlorosilyl-11-cyanoundecane and undecyltrichlorosilane (Gelest) during the preparation of the positively charged surfaces. Undecyltrichlorosilane has a CH\(_3\) end group that is uncharged. Reducing the amount of chargeable groups on the surface correspondingly reduces \(\sigma_{\text{bare}}\). The exact charge ratio on the surface could not be determined reliably because the ratio of charged:uncharged chlorosilanes in the bulk solution cannot be assumed to correspond to the ratio ultimately deposited on the surface. In addition, the preparation of the amine-terminated surfaces is lengthy, and small differences such as the amount of residual water in the solutions and the age of the stock solutions can lead to significant variations in the observed charge-inversion concentration. Here we only compare surfaces with different ratios of charged:uncharged chlorosilane that were prepared simultaneously from the same stock solutions, hence an increase in the charged:uncharged ratio is certain to correspond to an increase in \(\sigma_{\text{bare}}\).

Figures 6(a)–6(d) show an experiment where three positively charged surfaces with different \(\sigma_{\text{bare}}\) were charge inverted using the same bead and the quadrivalent ion [Fe(CN)\(_6\)]\(^{4-}\). Positively charged surfaces were prepared using only 1-trichlorosilyl-11-cyanoundecane (1:0) and ratios of 1-trichlorosilyl-11-cyanoundecane:undecyltrichlorosilane of 1:3 and 1:9. In this particular experiment, measurements were first done with a 1:3 surface [Fig. 6(a)], then with a 1:9 surface [Fig. 6(b)], and finally with a 1:0 surface [Fig. 6(c)]. The order of the measurements rules out that the observed trend is due to aging of the surfaces. Figure 6(d) shows the fitted values of \(F_{N0}(c)\) for all three surfaces, showing that decreasing \(\sigma_{\text{bare}}\) hinders charge inversion. The values obtained for \(c_0\) are 5, 17, and 74 \(\mu\)M for the 1:0, 1:3, and 1:9 surface, respectively.

Figure 6(e) shows the results of a control experiment where two different, nominally identical silica beads were charged inverted with [CoC\(_{12}\)H\(_{30}\)N\(_8\)]\(^{3+}\) and probed using a 1:9 and a 1:0 surface. The measured charge-inversion concentra-
obtained for the 1:0 surface is 320 μM. The 1:9 surface did not exhibit charge inversion at 1 mM [Fe(CN)₆]³⁻. Thus if the 1:9 surface can be charge inverted with [Fe(CN)₆]³⁻ ions, \(c_0\) is higher than 1 mM. Higher concentrations were not probed because \(\lambda\) becomes too short.

### VII. DISCUSSION

We first compare our experimental observations with the specific binding description as summarized by Eq. (2). Assuming constant \(\Delta \mu^0\), Eq. (2) predicts that \(c_0 \sim |\sigma_{\text{bare}}/Z|\) and is independent of \(\epsilon\). None of these trends agrees with the experiments. We instead observe a decrease of more than an order of magnitude in \(c_0\) when increasing \(Z\) from 3 to 4 [2], a decrease in \(c_0\) with increasing \(\sigma_{\text{bare}}\) instead of the predicted increase, and a sharp decrease in \(c_0\) with decreasing \(\epsilon\).

To reconcile the observations with Eq. (2) it is necessary to let the adsorption energy \(\Delta \mu^0\) depend on \(Z, \epsilon,\) and \(\sigma_{\text{bare}}\) and empirically fit its value for each individual measurement. While this approach lacks predictive power, some of the trends observed in the experiment could be rationalized in this way. For example, a more negative \(\Delta \mu^0\) might be expected for all ions when the dielectric constant is decreased since this affects ion solubility. The dielectric constant might similarly influence the hydrolysis of metal ions. Two aspects of the data call for a more universal explanation, however.

First, \(\Delta \mu^0\) is expected to depend critically on the specific chemical composition of the ions. Although some differences were observed with La³⁺, the measured \(c_0\) and its dependence on \(\epsilon\) was similar for three chemically very distinct ions with the same valence.

Second, the observed dependence of \(c_0\) on \(\sigma_{\text{bare}}\) implies that binding of the multivalent ions to the surface is cooperatively.

### TABLE I. Important parameters for the ion correlation model calculated using Eqs. (3)–(5) and the measured values of \(c_0\) (also shown) for the same ion with different values of \(\epsilon\).

<table>
<thead>
<tr>
<th>Ion</th>
<th>(c_0(\epsilon=80)) (μM)</th>
<th>(c_0(\epsilon=68)) (μM)</th>
<th>(c_0(\epsilon=54)) (μM)</th>
<th>(\sigma_{\text{bare}}) ((e/\text{nm}^2))</th>
<th>(\Delta \mu^0) (units of (kT))</th>
<th>(\mu_0(\epsilon=80)) (units of (kT))</th>
<th>(\mu_0(\epsilon=68)) (units of (kT))</th>
<th>(\mu_0(\epsilon=54)) (units of (kT))</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(CN)₆]⁴⁻</td>
<td>12</td>
<td>5</td>
<td>1</td>
<td>0.11</td>
<td>-4.1</td>
<td>-4.3</td>
<td>-5.2</td>
<td>-6.9</td>
</tr>
<tr>
<td>[Fe(CN)₆]³⁻</td>
<td>12</td>
<td>1</td>
<td></td>
<td>0.12</td>
<td>-4.0</td>
<td>-4.4</td>
<td>-5.4</td>
<td>-7.0</td>
</tr>
<tr>
<td>[Fe(CN)₆]⁴⁻</td>
<td>5</td>
<td>1</td>
<td></td>
<td>0.11</td>
<td>-3.9</td>
<td>-5.4</td>
<td>-7.0</td>
<td></td>
</tr>
<tr>
<td>[Fe(CN)₆]³⁻</td>
<td>120</td>
<td>18</td>
<td></td>
<td>0.17</td>
<td>-3.5</td>
<td>-3.3</td>
<td>-5.2</td>
<td></td>
</tr>
<tr>
<td>[CoC₆H₄(NO₃)₃]³⁺</td>
<td>220</td>
<td>88</td>
<td></td>
<td>-0.28</td>
<td>-2.2</td>
<td>-4.5</td>
<td>-5.4</td>
<td></td>
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<tr>
<td>[CoC₆H₄(NO₃)₃]³⁺</td>
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<td>14</td>
<td></td>
<td>-0.34</td>
<td>-1.9</td>
<td>-4.9</td>
<td>-7.7</td>
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</tr>
<tr>
<td>[CoC₆H₄(NO₃)₃]³⁺</td>
<td>88</td>
<td>14</td>
<td></td>
<td>-0.37</td>
<td>-1.6</td>
<td>-6.2</td>
<td>-8.0</td>
<td></td>
</tr>
<tr>
<td>[CoC₆H₄(NO₃)₃]³⁺</td>
<td>300</td>
<td>10</td>
<td></td>
<td>-0.50</td>
<td>-0.8</td>
<td>-6.2</td>
<td>-9.6</td>
<td></td>
</tr>
<tr>
<td>[Ru(NH₃)₃]³⁺</td>
<td>520</td>
<td>23</td>
<td></td>
<td>-0.43</td>
<td>-0.8</td>
<td>-5.6</td>
<td>-8.8</td>
<td></td>
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<tr>
<td>La³⁺</td>
<td>280</td>
<td>6</td>
<td></td>
<td>-0.63</td>
<td>-0.3</td>
<td>-7.0</td>
<td>-10.9</td>
<td></td>
</tr>
</tbody>
</table>
erative: increasing the density of surface charges facilitates charge inversion. This behavior is not captured by a simple chemical binding picture. This remains true even if a more sophisticated description of the surface is introduced. For example, the surface can be modelled as consisting of discrete sites where multivalent ions compete with other charge-determining ions. Such a model yields an equation similar to Eq. (2) but with a prefactor that is independent of \( \sigma_{\text{bare}} \). That is, it still does not exhibit cooperativity.

We now compare the observations with the ion correlation theory of Eqs. (3)–(5). The latter predicts that 
\[ \mu_c = -\sqrt{n(\sigma_{\text{bare}}/\epsilon)} \] 
and this expression captures very well the direction (increase or decrease) and relative magnitude of the dependence of \( c_0 \) on these parameters.

The experimental data permit a more quantitative self-consistency test of this theory. Two unknown parameters enter the model: the surface-charge density at charge inversion, \( \sigma_{\text{bare}}(c_0) \), and the residual chemical interaction, \( \Delta \mu^0 \). Two measurements carried out under slightly different conditions can be used for extracting values for these parameters. We previously showed in this manner that varying \( Z \) while keeping the chemical structure constant yields results consistent with \( \Delta \mu^0 = 0 \) [2].

A similar procedure can be used for the measurements at different values of \( \epsilon \) presented here. Assuming that \( \sigma_{\text{bare}} \) and \( \Delta \mu^0 \) do not depend on \( \epsilon \), their values can be deduced from consecutive measurements using the same ion and solvents with different \( \epsilon \). The numerical results of this procedure are summarized in Table 1, together with the corresponding calculated values of \( \mu_c \). In those cases where three values of \( \epsilon \) were measured, fits were performed pairwise to extract separate estimates of \( \sigma_{\text{bare}} \) and \( \Delta \mu^0 \); the results are consistent within experimental scatter.

We first focus on the results for charge inversion of a silica bead by trivalent positive ions. The fitted values of \( \Delta \mu^0 \) are in the range \(-0.5kT\) to \(-2.2kT\). For comparison, the corresponding values of \( \mu_c \) are in the range \(-4.5kT\) to \(-10.9kT\). This implies that spatial correlations between multivalent ions are largely sufficient to account for charge inversion. Results for the three different trivalent positive ions are similar, re-iterating that, in spite of anomalies observed with \( \text{La}^{3+} \), the chemical composition of these ions does not appear to play a dominant role in determining \( c_0 \). Figure 8(a) plots the measured values of \( c_0 \) as a function of \( \epsilon \) for the different experiments, and shows that all of our measurements for silica surfaces are consistent with \( \sigma_{\text{bare}} = -0.5 \; \epsilon / \text{nm}^2 \) and \( \Delta \mu^0 = -1kT \). Taken together, these observations lend further support to the proposal that a spatial interaction between multivalent ions is the driving mechanism behind charge inversion.

Results for the amine-terminated surfaces are not as clear cut. The calculated values of \( \Delta \mu^0 \) for charge inversion of the amine-terminated surface by trivalent and quadrivalent negative ions are significantly larger than \( kT \) and comparable in magnitude to \( \mu_c \). Figure 8(b) shows that the values of \( c_0 \) for these measurements can be described by Eq. (3) using \( \sigma_{\text{bare}} = 0.14 \; \epsilon / \text{nm}^2 \) and \( \Delta \mu^0 = -3.6kT \). In terms of Eq. (3), this suggests that spatial correlations between multivalent ions do not fully account for the observed charge inversion in this case, and that specific binding also plays a role.

One possible reason for this discrepancy is that the calculated values of \( \sigma_{\text{bare}} \) of the amine-terminated surfaces correspond to the lower end of the range of validity of the inequality \( \Gamma \gg 1 \). A similar trend was observed in measurements where \( Z \) was varied with low surface-charge densities [2]. Another possible reason is that in the theoretical descriptions discussed here, the charge on the surface is modelled as being continuously distributed whereas real surfaces consist of discrete chemical groups. This disorder can potentially facilitate charge inversion [28,29]. The relative importance of this disorder is expected to increase with decreasing \( \sigma_{\text{bare}} \).

Some caution is necessary in drawing conclusions from the quantitative analysis above, however. If regulation of the surface charge plays a significant role, \( \sigma_{\text{bare}} \) depends on the ion concentrations and thus on \( c_0 \). The analysis instead assumes that \( \sigma_{\text{bare}} \) remains constant. Similarly, both \( \sigma_{\text{bare}} \) and \( \Delta \mu^0 \) can depend on \( \epsilon \) [30], introducing errors in the quantitative comparison. The degree of consistency between the three calculated values of \( \sigma_{\text{bare}} \) and \( \Delta \mu^0 \) for the measurements with three values of \( \epsilon \) suggests that treating \( \sigma_{\text{bare}} \) and \( \Delta \mu^0 \) as constants is at least approximately valid, however. To describe the behavior of \( F_0 \) away from \( c_0 \), regulation of the surface charge has to be considered within the theory. Elucidating the interplay between disorder, regulation and correlations remains an important theoretical challenge.

In summary, we have performed a systematic study of charge inversion by multivalent ions using atomic force spectroscopy. At long range this technique gives a direct, unambiguous measurement of the polarity of the surface being probed. Measurements at shorter range show an additional attractive component of the force, corresponding to constant-potential boundary conditions. We measured the dependence of the charge-inversion concentration on valence, chemical composition, dielectric constant, and surface-charge density, the latter indicating that multivalent ion adsorption is cooperative. These observations are remarkably consistent with a very straightforward description of charge inversion in terms of spatial interactions between multivalent
ions in the Stern layer [16]. To our knowledge, no existing description based on specific adsorption provides a similar degree of agreement, even at a qualitative level. A direct experimental proof of the correlation mechanism, via direct determination of the spatial correlations between multivalent ions at the surface, would be highly desirable.

[21] Sum of metal ion radius and ligand (H₂O, NH₃, CN⁻) diameter. The radii are comparable (within 4%) to crystallographic data.
[24] Measurements were done at pH less than the first hydrolysis constant of La³⁺; J. Burgess, Metal Ions in Solution (Ellis Horwood, Chichester, England, 1979), Chap. 9.

ACKNOWLEDGMENTS

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