Macroscopic surface charges from microscopic simulations

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Attaining accurate average structural properties in a molecular simulation should be considered a prerequisite if one aims to elicit meaningful insights into a system’s behavior. For charged surfaces in contact with an electrolyte solution, an obvious example is the density profile of ions along the direction normal to the surface. Here we demonstrate that, in the slab geometry typically used in simulations, imposing an electric displacement field \( D \) determines the integrated surface charge density of adsorbed ions at charged interfaces. This allows us to obtain macroscopic surface charge densities irrespective of the slab thickness used in our simulations. We also show that the commonly used Yeh-Berkowitz method and the ‘mirrored slab’ geometry both impose vanishing integrated surface charge density. We present results both for relatively simple rocksalt (111) interfaces, and the more complex case of kaolinite’s basal faces in contact with aqueous electrolyte solution.

I. INTRODUCTION

Charged surfaces in contact with solution are commonplace in fields as diverse as colloid science, geology and energy materials.1–7 As such, there is great interest in using molecular simulations to probe the details of these systems at the microscopic scale. However, the long-ranged nature of electrostatic interactions, and the relatively small system sizes typically afforded by molecular simulations can have severe consequences for simulated observables.8–12 The purpose of this article is to demonstrate how commonly used simulation approaches lead to qualitatively incorrect descriptions of ion adsorption at charged interfaces. We will also extend the ideas of previous works12–15 to not only correct for small system sizes, but to understand why other methods fail in a dramatic fashion. In fact, this simply amounts to setting the electrostatic boundary conditions appropriately; as this is relatively straightforward to do in existing simulation packages,16 it is hoped that the results presented here—along with those in Refs. 12–15—will be useful to the simulation community in modeling charged solid/liquid interfaces.

To illustrate one of the main challenges faced when simulating charged interfacial systems, it is perhaps useful to first discuss what the physical scenario is that we aim to describe. For simplicity, we only explicitly consider surface charge originating from polar crystallographic axes, although it is important to note that other mechanisms are possible e.g. protonation/deprotonation of functional groups; our results are directly relevant to such cases too. To this end, consider the situation depicted in Fig. 1(a). Here, a macroscopic single crystal exposing polar facets—resulting from the termination of the crystal along a crystallographic direction comprising alternating planes of opposite charge—is immersed in an electrolyte solution. It is well established that such polar crystal terminations are inherently unstable, and require a polarity compensation mechanism.15,17–20 In this article, we will focus on the case where adsorption of charge from the external environment stabilizes the crystal. Specifically, we expect counterions from solution to adsorb to the crystal’s surfaces such that the integrated charge density over an interfacial region, e.g.,

\[
\sigma^{(macro)} = \int_{int^+} dz \, n(z),
\]

provides the appropriate polarity compensation. In Eq. 1, \( n \) is the charge density profile perpendicular to the interface, which we take to define the \( z \) direction, and the integration is understood to be taken over the interfacial region corresponding to the positively charged crystal surface. A similar definition holds for \( \sigma^{(macro)} \). The exact value of \( \sigma^{(macro)} \) depends upon the in-plane charge density \( \sigma_0 \) and the crystal structure (see Fig. 1). For example, in the case of rocksalt (111), \( \sigma^{(macro)} \approx \mp \sigma_0/2 \), while for the (0001) surfaces of wurtzite isomorphs, \( \sigma^{(macro)} \approx \mp \sigma_0/4 \). A reasonable goal for a molecular simulation is to obtain an integrated interfacial charge density \( \sigma^{(sim)} \approx \sigma^{(macro)} \) that well approximates the macroscopic sample of interest.

A typical classical molecular dynamics simulation comprises \( 10^2–10^5 \) molecules. This is obviously far smaller than what is found in the macroscopic sample sizes that experiments can probe. To avoid artificially large surface-to-volume ratios or degrees of interfacial curvature, periodic boundary conditions (PBC) are typically applied, in which the system is periodically replicated in all three dimensions.21,22 Two typical geometries of a simulation cell used to study interfacial systems under PBC are shown in Fig. 1. The first of these, shown in Fig 1 (b), and simply referred to as the slab geometry, consists of a single slab of solid material with thickness \( w \) centered at \( z = 0 \) and surrounded on either side by electrolyte solution. The slab itself comprises alternating planes of opposite charge, which at present are simply taken to have an equidistant spacing; a simple generalization to

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FIG. 1. Schematic of polarity compensation from the solution environment. (a) The system of interest is a single crystal that predominantly exposes polar crystal facets with surface charge density ±σ₀. The thickness of the crystal W is macroscopic in extent. In the absence of other mechanisms, counterions will adsorb from solution to stabilize the crystal such that the integrated surface charge density is σ_(macro) (see Eq. 1), as represented by the dotted line. (b) Simulation cell employing the slab geometry often used in simulations to study interfacial systems. The simulation cell is periodically replicated in all three dimensions. The thickness of the slab w is much smaller than W. The integrated surface charge density σ_(sim) will depend upon the electrostatic boundary conditions employed. (c) Simulation cell for the mirrored slab geometry. Here two slabs with dipole moments pointing in opposite directions confine an electrolyte solution. Periodic images are separated by vacuum. The simulation cell is periodically replicated in all three dimensions. In both (b) and (c), L denotes the length of the simulation cell in the direction perpendicular to the surface plane, which is taken to be z.

more complex scenarios will be presented in Sec. III. The total extent of the simulation cell along z is L, with the boundaries of the cell at z = ±L/2. We stress that we have chosen to work with the crystal in the center of the simulation cell for convenience, but that the results can be generalized to the case where the crystal straddles the cell boundary. The second simulation geometry considered, the mirrored slab geometry, is shown in Fig. 1 (c). In this case, one slab is centered at zm < (L − w)/2, and its mirror image is centered at −zm. The region between the slabs is occupied by an electrolyte solution, while the regions exterior to the slabs (that separate periodic images) are vacuum. In what follows we will investigate the adsorption of ions from solution to polar surfaces in these two common simulation geometries. We will demonstrate that the mirrored slab geometry amounts to working with boundary conditions that enforce σ_(sim) ≈ 0, a surely untenable situation. In contrast, with an appropriate choice of boundary conditions, we will show that the slab geometry yields σ_(sim) ≈ σ_(macro), even with relatively small simulation cells.

The remainder of the article is organized as follows. First, we will present a brief overview of the finite field approach and its application to polar surfaces. This amounts to manipulating the electrostatic boundary conditions. We will then present results for a simple rocksalt system that demonstrates the severe implications that the boundary conditions have on ion adsorption behavior. In Sec. III we will show how this framework can be applied to more complex systems, using kaolinite’s basal surfaces as an example. We will end with a summary and outlook for future directions.

II. CONTROLLING SURFACE CHARGE WITH FINITE FIELDS

The difficulties in simulating systems like those shown in Fig. 1 originate from the long-ranged nature of electrostatic interactions. In order to accurately compute Coulombic forces, methods based on Ewald sums are typically used. Let \( H_{\text{PBC}} \) denote a Hamiltonian that includes electrostatic interactions computed with an Ewald method (under the so-called ‘tin foil boundary conditions’), along with any non-electrostatic interactions. For the slab geometry, a natural question arises: How quickly do simulations converge to the limit \( L \to \infty \)? With the implicit assumption that w is held fixed, it has long been known that the answer is “not very”. To avoid large values of L or computationally expensive two-dimensional versions of Ewald sums, Yeh and Berkowitz (YB) devised a simple correction scheme in which the system’s Hamiltonian is given by

\[
H_{\text{YB}} = H_{\text{PBC}} + 2\pi \Omega P^2,
\]
where \( P \) is the \( z \) component of the system’s instantaneous polarization, and \( \Omega \) is the volume of the simulation cell. (In our formulation, we use a unit system in which \( 4\pi \epsilon_0 = 1 \), where \( \epsilon_0 \) is the permittivity of free space.) The YB approach has become one of the most widely used methods for simulating slab systems. In the mirrored slab geometry, \( \langle P \rangle \approx 0 \). It could then be argued, at least on average, that the YB correction term is redundant. Indeed, the mirrored slab geometry has been proposed as a means to correct for unphysical long-ranged fields arising from finite polar surfaces.\(^{26–31}\) As Fig. 1 makes clear, however, a more pertinent question for the current purpose is: \textit{How quickly do simulations converge to the limit where both} \( L \) \text{ and} \( w \) \text{ are macroscopic in extent?}

In Fig. 2 we show how \( |\sigma^{(\text{sim})}_\pm| \) varies for rocksalt (1 1 1), in contact with a concentrated aqueous NaCl solution, as \( n = w/R \) is varied. (The slab comprises \( n + 1 \) layers separated by a distance \( R \).) Here we can see that when using \( \mathcal{H}_{\text{PBC}} \), \( |\sigma^{(\text{sim})\pm}| \) approaches \( |\sigma^{(\text{macro})\pm}| \) from below as \( n \) increases. In other words, for small \( n \) the crystal’s surface charge is \textit{underscreened}. To fix this problem of underscreening, Zhang and Sprik (ZS) proposed the application of an appropriate electric field \( E \) or electric displacement field \( D \) across the simulation cell. This is achieved with the finite field approach, as prescribed by the Hamiltonian

\[
\mathcal{H}_E = \mathcal{H}_{\text{PBC}} - \Omega EP \quad \text{(constant} \ E \text{),} \tag{3}
\]

or

\[
\mathcal{H}_D = \mathcal{H}_{\text{PBC}} + \frac{\Omega}{8\pi}(D - 4\pi P)^2 \quad \text{(constant} \ D \text{).} \tag{4}
\]

In addition to charged interfacial systems,\(^{12–15,32,33}\) the finite field approach has been used to investigate the response of both dielectrics\(^{23,34–37}\) and ionic conductors.\(^{38,39}\) For a metal in contact with liquid electrolyte, it has also been shown to give results indistinguishable from 2D Ewald.\(^{40}\) Moreover, although Eqs. 3 and 4 were first derived on thermodynamic grounds,\(^{23}\) they are full microscopic Hamiltonians that can also be derived from an extended Lagrangian based on arguments of theoretical mechanics.\(^{41}\) See Ref. 42 for a recent review. From Eq. 3, it can be seen that using \( \mathcal{H}_{\text{PBC}} \) on its own is equivalent to imposing \( E = 0 \). ZS originally considered a situation in which \( n = 1 \) with increasing \( R \), for which the rationale of imposing an \( E \) or \( D \) field was simple; underscreening leads to an erroneous electric field inside the slab, which is removed by imposing an appropriate field. In this study, we will refer to these fields as \( E^{(ZS)} \) and \( D^{(ZS)} \). While \( E^{(ZS)} \) is generally found by trial-and-error, \( D^{(ZS)} \) can be obtained \textit{a priori} provided the structure of the crystal and \( \sigma_0 \) are known. We will discuss this point in more detail below. Both \( E^{(ZS)} \) and \( D^{(ZS)} \) enforce the average field inside the slab to vanish.

This approach was extended to polar crystal surfaces—specifically rocksalt (1 1 1)—by Sayer \textit{et al.},\(^{13,14}\) where \( E^{(ZS)} \) and \( D^{(ZS)} \) were argued to decouple the two interfaces present in the slab geometry [see Fig. 1 (b)] such that the double layer capacitance could be measured with small simulation cells. A rather striking observation from Refs. 13 and 14, however, is that in the ZS approach the surface charge depends on \( n \):

\[
\sigma^{(\text{sim},ZS)}_\pm = \frac{n + 1}{n} \sigma^{(\text{macro})\pm}. \tag{5}
\]

Thus, while \( \lim_{n \to \infty} \sigma^{(\text{sim},ZS)}_\pm = \sigma^{(\text{macro})\pm} \), significant deviations are expected when \( n \) is small. We mentioned above that \( D^{(ZS)} \) can be established \textit{a priori} if certain properties of the system are known. For rocksalt (1 1 1),\(^{13,14}\)

\[
D^{(ZS)} = 4\pi n + 1 \sigma^{(\text{macro})\pm} \equiv 4\pi \sigma^{(\text{sim},ZS)}_\pm. \tag{6}
\]

The choice of \( \sigma^{(\text{macro})\pm} \) or \( \sigma^{(\text{macro})\pm} \) depends upon the direction of the crystal’s polarization \( P_{\text{abl}} \), with \( P_{\text{abl}} > 0 \) corresponding to \( \sigma^{(\text{macro})\pm} \) and \textit{vice versa}. The results for \( |\sigma^{(\text{sim})\pm}| \) obtained with \( D = D^{(ZS)} \) are shown in Fig. 2, along with the theoretical prediction given by Eq. 5. As expected, \( |\sigma^{(\text{macro})\pm}| \) is approached from above, and the results appear to be converging for large \( n \).

The ZS approach was designed as a means to compute the double layer capacitance with relatively small simulation cells, and has enjoyed success not only with classical force field models,\(^{12,13,15,33,40}\) but also with \textit{ab initio} approaches.\(^{14,32}\) Moreover, \( n = 1 \) yields \( \sigma^{(\text{sim},ZS)}_\pm \approx
\[ \pm \sigma_0, \text{ which is appropriate if one is interested in modeling charged surfaces that arise from e.g. protonation/deprotonation of surface groups. (See also Ref. 43 for an alternative approach for tackling the n = 1 system.) To obtain } \sigma_{\pm}^{(\text{sim})} \approx \sigma_{\pm}^{(\text{macro})} \text{ for polar surfaces, however, it is clear from Fig. 2 that a relatively large number of crystal layers is required. This was the approach we adopted in Ref. 15 in our study of AgI in contact with aqueous solution.}^{44} \text{ Should this be necessary? Eq. 6 suggests an inextricable link between } D \text{ and } \sigma_{\pm}^{(\text{sim})}: \]

The value of \( D \) directly determines \( \sigma_{\pm}^{(\text{sim})} \), independent of \( L \).

This is the central message of this article. It is important to note that implicit in this statement is that the electric field between periodic replicas is assumed to vanish; this is ensured in our simulations by the fact that the slab is surrounded by electrolyte. While this relationship between \( D \) and \( \sigma_{\pm}^{(\text{sim})} \) can be inferred from previous studies\cite{12,14}—where derivations can also be found—it has only been used to impose vanishing average electric field inside the slab as a means to compute the double layer capacitance. Here we provide empirical support showing this relationship holds across a range of values for \( D \), and demonstrate its significance beyond calculating the double layer capacitance. From this perspective, obtaining \( \sigma_{\pm}^{(\text{sim})} \approx \sigma_{\pm}^{(\text{macro})} \) is then a simple case of setting the displacement field accordingly, i.e.,

\[ D^{(\text{macro})} = 4\pi \sigma_{\pm}^{(\text{macro})}. \] (7)

Results from simulations with \( D = D^{(\text{macro})} \) are shown in Fig. 2, where it is seen that \( |\sigma_{\pm}^{(\text{sim})}| \approx |\sigma_{\pm}^{(\text{macro})}| \) is an excellent approximation over the range of \( n \) investigated.

This relationship has a striking implication for the behavior of both the YB approach and the mirrored slab geometry. It has been previously noted that \( \mathcal{H}_Y \) and \( \mathcal{H}_D \) with \( D = 0 \) are formally equivalent,\cite{12} and one might therefore expect that \( \sigma_{\pm}^{(\text{sim})} \approx 0 \). Our results in Fig. 2 confirm this notion and, along with the results using \( D = D^{(\text{ZS})} \) and \( D = D^{(\text{macro})} \), provide convincing evidence that the value of \( D \) directly determines \( \sigma_{\pm}^{(\text{sim})} \). For the mirrored slab geometry, \( \mathcal{H}_{\text{PBC}} \) on its own is used. Recall that this corresponds to \( E = 0 \) (see Eq. 3). Thus, if \( \langle P \rangle \approx 0 \) then \( \langle D \rangle = E + 4\pi \langle P \rangle \approx 0 \), and the mirrored slab geometry corresponds, on average, to \( D = 0 \). We have previously shown that for AgI (0001) in contact with pure water, the mirrored slab geometry and regular slab geometry with \( D = 0 \) give similar electrostatic potential profiles, and orientation statistics for the interfacial water molecules.\cite{15} For the rocksalt (111) surface in contact with electrolyte considered here, Fig. 2 shows that with the mirrored slab geometry, \( |\sigma_{\pm}^{(\text{sim})}| \approx 0 \) over the range of \( n \) considered. (The Cl\textsuperscript{-} planes are exposed to solution.) This strongly suggests that both \( \mathcal{H}_Y \) and the mirrored slab geometry are unsuitable for modeling systems like those depicted in Fig. 1 (a).

### III. APPLICATION TO KAOLINITE’S BASAL SURFACES

The results presented so far demonstrate that \( \sigma_{\pm}^{(\text{macro})} \) can be obtained for any value of \( n \) provided one uses the appropriate electrostatic boundary conditions. This is achieved most straightforwardly by setting \( D = 4\pi \sigma_{\pm}^{(\text{macro})} \) in \( \mathcal{H}_D \) (Eq. 4). So far, we have only tackled the relatively simple rocksalt (111) surface. Here we demonstrate the relevance of the principles established in Sec. II to a more complex system, namely the basal surfaces of kaolinite, an aluminosilicate clay mineral. These surfaces are widely studied with molecular simulation owing to their importance in ice nucleation and geochemistry.\cite{29,45–50} To proceed, we need to establish an estimate for \( \sigma_{\pm}^{(\text{macro})} \) for the crystal structure shown in Fig 3 (a). To this end, we will simply use established results from the solid state community. For a detailed discussion of the underlying theory, we refer the reader to the review by Goniakowski et al.\cite{19}

While kaolinite presents a complex crystal structure, an estimate for \( \sigma_{\pm}^{(\text{macro})} \) can in fact be determined in a rather simple fashion, and furthermore highlights an essential aspect of the theory of polar surfaces: The dipole moment \( \mu_B \) of the bulk repeat unit determines \( \sigma_{\pm}^{(\text{macro})} \). This means that \( \sigma_{\pm}^{(\text{macro})} \) may depend upon how the bulk crystal structure is terminated, which can be important for materials such as TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} and SrTiO\textsubscript{3}. For kaolinite, however, it is natural to cleave its basal surfaces such that only relatively weak hydrogen bonds are broken, as indicated by the gray dotted line in Fig. 3 (a). With the CLAYFF force field\cite{52} used in this study, we find \( |\mu_B| \approx 14.1 \text{ D} \). For comparison, the rocksalt (111) surface with the Joung-Cheatham force field\cite{52} gives \( |\mu_B| \approx 7.8 \text{ D} \). Denoting the volume of the repeat unit as \( \Omega_0 \), our estimate for \( \sigma_{\pm}^{(\text{macro})} \) is then simply given by

\[ \sigma_{\pm}^{(\text{macro})} = \frac{\pm |\mu_B|}{\Omega_0}. \] (8)

It is straightforward to verify that for rocksalt (111), Eq. 8 recovers \( \sigma_{\pm}^{(\text{macro})} = \mp \sigma_0/2 \approx \mp 3.6 \text{ e/\text{nm}^2} \). For kaolinite we find \( \sigma_{\pm}^{(\text{macro})} \approx \mp 0.89 \text{ e/\text{nm}^2} \). While we therefore expect quantitative differences between rocksalt (111) and kaolinite's basal surfaces, we nonetheless expect a comparable (i.e., same order of magnitude) coverage of adsorbed counterions at the two surfaces. We note in passing that Eq. 8 states that \( \sigma_{\pm}^{(\text{macro})} \) is determined by properties of the bulk repeat unit, and is not related to any surface dipole that may exist.

Performing simulations for a single sheet of kaolinite with its basal surfaces in contact with aqueous solution, and its atoms fixed in their bulk crystal lattice positions, corroborates the findings presented in Sec. II: \( |\sigma_{\pm}^{(\text{sim})}| \approx 0.89 \text{ e/\text{nm}^2} \) using \( \mathcal{H}_E \) and \( E = 0 \); \( |\sigma_{\pm}^{(\text{sim})}| \approx 0.00 \text{ e/\text{nm}^2} \) using \( \mathcal{H}_D \) and \( D = 0 \); and \( |\sigma_{\pm}^{(\text{sim})}| \approx \sigma_{\pm}^{(\text{macro})} \approx \)
FIG. 3. Application to kaolinite’s basal surfaces in contact with aqueous NaCl solution. (a) The bulk crystal structure of kaolinite comprises layers of Al₂Si₂O₅(OH)₄. The basal surfaces are generated by cleaving relatively weak interlayer hydrogen bonds, as indicated by the gray dotted lines. The black lines delineate the bulk repeat unit. (b) Number density profiles ρ of Na⁺ and Cl⁻ obtained at D = 0. The gray shaded area approximately indicates the region occupied by kaolinite. The corresponding results obtained at E = 0 and D = D\textsuperscript{(macro)} are shown in (c) and (d), respectively. The blue arrows indicate the orientation of the crystal.

0.89 e/\text{nm}^2 using \( \mathcal{H}_D \) and \( D = D\textsuperscript{(macro)} \) as given by Eqs. 7 and 8. Perhaps more striking, however, are the ion density profiles, as shown in Figs. 3 (b)-(d). Here we see that simulations using \( D = 0 \) give qualitatively incorrect results, with essentially no ion adsorption observed. This result is broadly in line with Ren et al., who used the mirrored slab geometry, and even reported slightly more favorable adsorption of cations vs. anions at kaolinite’s positive (0001) surface.\(^{30}\) (Results from the mirrored slab geometry are shown in Fig. S1, and are in good agreement with those from simulations using \( D = 0 \).) In contrast, with both \( E = 0 \) and \( D = D\textsuperscript{(macro)} \) we see behavior in line with physical intuition, with Na⁺ and Cl⁻ ions adsorbed to the negative (0001) and positive (0001) surfaces, respectively. These results are also consistent with Vasconcelos et al.,\(^{49}\) who investigated ion adsorption at kaolinite’s basal faces with a standard Ewald method. Moreover, performing simulations with \( E = 0 \) for two and three sheets of kaolinite yields \( |\sigma\textsuperscript{\text{sim}}_\pm| \approx 0.88 e/\text{nm}^2 \) in both cases suggesting that, even with a single sheet of kaolinite, results are sufficiently converged. On the whole, for both the rocksalt (1 1 1) and kaolinite systems, we find \( E = 0 \) simulations yield largely satisfactory results. How quickly results converge as \( n \) increases, however, appears to be system-dependent.

Throughout this article, we have deliberately avoided detailed theoretical discussions, instead choosing to focus on empirically demonstrating how different electrostatic boundary conditions affect \( \sigma\textsuperscript{\text{macro}}_\pm \). Nonetheless, we end this section with a couple of comments concerning the underlying theory. First, the relation \( D = 4\pi\sigma\textsuperscript{\text{sim}}_\pm \) can be interpreted as a statement that the ‘virtual electrodes’ directly influence the behavior of the system at the cell boundaries (see Refs. 12 and 23). In the case that an electrolyte—which has unit polarizability—straddles the cell boundary, its polarization is then immediately determined: \( 4\pi P = D \). The surface charge density in the double layer then follows from basic electrostatic arguments i.e., \( 4\pi\sigma\textsuperscript{\text{sim}}_\pm = 4\pi P = D \). Crucial to this argument is that the ions are included in the polarization. Second, if \( D = D\textsuperscript{(ZS)} \) enforces a vanishing average electric field inside the crystal, what is the effect of \( D = D\textsuperscript{(macro)} \)? Enforcing \( \sigma\textsuperscript{\text{sim}}_\pm = \sigma\textsuperscript{\text{macro}}_\pm \) removes the linear component of the electrostatic potential \( \phi(z) \) in the crystal’s interior e.g. in the case of rocksalt (1 1 1), \( \phi(z) = \phi(z + 2R) \), whereas \( D = D\textsuperscript{(ZS)} \) imposes \( \phi(-w/2) = \phi(w/2) \). Thus while with \( D = D\textsuperscript{(macro)} \) an electrostatic potential difference across the crystal remains, it does not grow with \( w \), and avoids the so-called ‘polar-catastrophe’.\(^{17–20}\)

In Fig. 4 we present \( \phi(z)\textsuperscript{\text{ZS}} \) for both the rocksalt (1 1 1) system with \( n = 5 \), and the kaolinite system with three sheets of crystal. In the case of the former [Fig. 4 (a)], \( \phi \) exhibits a significant linear component within the crystal’s interior, which is indeed removed by imposing \( D = D\textsuperscript{(ZS)} \). In contrast, for kaolinite [Fig. 4 (b)] we see that \( \phi \) is broadly similar between \( E = 0 \) and \( D = D\textsuperscript{(macro)} \), which is reflected in the similar values for \( \sigma\textsuperscript{\text{sim}}_\pm \) reported above. Importantly, negligible linear component in \( \phi \) is observed, giving us confidence that Eq. 8 provides a good estimate for \( \sigma\textsuperscript{\text{macro}}_\pm \), even for complex systems like kaolinite.

IV. SUMMARY AND OUTLOOK

In this article, we have investigated the effect of different electrostatic boundary conditions on simulated observables such as ion distributions and integrated surface charge densities for polar crystal surfaces in contact with aqueous solution. We have shown that on average, the mirrored slab geometry with \( E = 0 \) and slab geometry with \( D = 0 \) give similar, but intuitively incorrect, results. Specifically, such simulation conditions impose a vanishing integrated surface charge density. Using results from studies on polar surfaces by the solid state community,\(^{19}\) combined with recent developments in performing molecular dynamics simulations at constant \( E \) and \( D\textsuperscript{(macro)} \), we have shown that one can obtain sensible surface charge densities with relatively small simulation cells. We also showed how this approach can be applied to complex systems such as clay minerals. Although we have previously demonstrated the use of the finite field approach for ice formation at AgI’s polar surfaces,\(^{15}\) for liquid/solid interfaces they have primarily been used as a tool to compute the double layer capacitance. While undoubtedly an important property, what this work makes clear is that this framework also provides a means to understand the ef-
effects of electrostatic boundary conditions on simulated observables of general importance, such as average structural properties.

We are of course ultimately interested in ‘correct’ rather than ‘sensible’ results. Neglecting issues concerning the underlying simple point charge force fields (including their appropriateness for calculating the bulk polarization in Eq. 8, see e.g. Ref. 54), those presented here should be a good approximation for polar crystal surfaces with a bulk-terminated crystal structure, and where all polarity compensation arises by adsorption of ions from solution. Allowing for surface relaxation will likely manifest itself as a relatively small perturbation.\textsuperscript{15} In contrast, ascertaining the relative importance of different polarity compensation mechanisms—such as non-stoichiometric or electronic reconstruction—remains an open and challenging question. Addressing this issue will be a key step in establishing what the stable structures of polar crystal surfaces actually are in a solution environment. This will likely be important in the future development of crystal structure prediction approaches as they try to incorporate more information regarding the influence of the solution environment.\textsuperscript{55}

V. METHODS

All simulations used the SPC/E water model,\textsuperscript{56} whose geometry was constrained using the RATTLE algorithm\textsuperscript{57} and the Joung-Cheatham NaCl force field.\textsuperscript{52} For simulations involving kaolinite, the CLAYFF force field was used.\textsuperscript{51} Lorentz-Berthelot mixing rules were used to compute Lennard-Jones interactions between different species. Dynamics were propagated using the velocity Verlet algorithm with a time step of 2 fs. The temperature was maintained at 298 K with a Nosé-Hoover chain;\textsuperscript{58,59} with a damping constant 0.2 ps. The particle-particle particle-mesh Ewald method was used to account for long-ranged interactions,\textsuperscript{60} with parameters chosen such that the root mean square error in the forces were a factor 10\textsuperscript{5} smaller than the force between two unit charges separated by a distance of 0.1 nm.\textsuperscript{61} A cutoff of 1 nm was used for non-electrostatic interactions. For results in the main article, the LAMMPS simulation package was used throughout.\textsuperscript{62} For simulations with a $D$ field, the implementation given in Ref. 39 was used. Results from simulations using the GROMACS 4 simulation package\textsuperscript{63} are presented in Fig. S2.

For the results presented in Fig. 2, the electrolyte comprised 600 water molecules and 20 NaCl ion pairs. The crystal consisted of alternating layers of Na\textsuperscript{+} and Cl\textsuperscript{−} ions, separated by $R = 0.1628$ nm, and each layer comprised 16 ions. The lateral dimensions of the simulation cell were $L_x = 1.5952$ nm and $L_y = 1.3815$ nm along $x$ and $y$, respectively. In the slab geometry with $n = 3$, the length of the simulation cell along $z$ was $L_z = 9.4841$ nm, and $L$ was increased with $n$ accordingly e.g. for $n = 5$, $L$ was increased by $2R$. For the mirrored slab geometry, $L$ was double that of the corresponding simulation in the slab geometry. Each simulation was 10 ns long post equilibration.

For results presented in Fig. 3, the electrolyte comprised 605 water molecules and 5 NaCl ion pairs. The bulk kaolinite structure was taken from Ref. 50. An orthorhombic simulation cell was used with $L_x = 1.5462$ nm and $L_y = 1.7884$ nm. For simulations with a single sheet $L = 7.5$ nm, while for simulations with two and three sheets, $L = 8.2162$ nm and 8.9323 nm, respectively. Simulations were 100 ns long post equilibration. Results presented in Fig. 4 (b) used the same settings, except simulations were 20 ns long post equilibration.

![Electrostatic potential profiles](image)
SUPPLEMENTARY MATERIAL

Supplementary Material includes results from simulations for kaolinite in a mirrored slab geometry, along with results for rocksalt (1 1 1) using the GROMACS simulation package.

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DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available within the article and its supplementary material. Input files for the simulations are openly available at the University of Cambridge Data Repository, https://doi.org/10.17863/CAM.56629.

1S. L. Swartzen-Allen and E. Matijevic, Chem. Rev. 74, 385 (1974).
2G. Sposito, N. T. Skipper, R. Sutton, S.-h. Park, A. K. Soper, and J. A. Greathouse, Proc. Natl Acad. Sci. USA 96, 3358 (1999).
3K. Xu, Chem. Rev. 104, 4303 (2004).
4K. Xu, Chem. Rev. 114, 11503 (2014).
5M. Salanne, B. Rotenberg, K. Naoi, K. Kaneko, P.-L. Taberna, C. P. Grey, B. Dunn, and P. Simon, Nat. Energy 1, 1 (2016).
6D. Mora-Fonz, T. Lazauskas, M. R. Farrow, C. R. A. Catlow, S. M. Woodley, and A. A. Sokol, Chem. Mater. 29, 5306 (2017).
7R. Hartkamp, A.-L. Biance, L. Fu, J.-F. Dufrêne, O. Bonhomme, and L. Joly, Curr. Opin. Colloid Interface Sci. 37, 101 (2018).
8G. Hummer, L. R. Pratt, and A. E. García, J. Phys. Chem. 100, 1206 (1996).
9C.-L. Yeh and M. L. Berkowitz, J. Chem. Phys. 111, 3155 (1999).
10P. H. Hünenberger and J. A. McCammon, J. Chem. Phys. 110, 1856 (1999).
11S. J. Cox and P. L. Geissler, J. Chem. Phys. 148, 222823 (2018).
12C. Zhang and M. Sprik, Phys. Rev. B 94, 245309 (2016).
13T. Sayer, C. Zhang, and M. Sprik, J. Chem. Phys. 147, 104702 (2017).
14T. Sayer, M. Sprik, and C. Zhang, J. Chem. Phys. 150, 041716 (2019).
15T. Sayer and S. J. Cox, Phys. Chem. Chem. Phys. 21, 14546 (2019).
16Source code that implements the finite field approach in LAMMPS is freely available at https://github.com/uccasco/FiniteFields.
17P. Tasker, J. Phys. C: Solid State Phys. 12, 4977 (1979).
18R. Nosker, P. Mark, and J. Levine, Surf. Sci. 19, 291 (1970).
19J. Goniakowski, F. Finocchi, and C. Noguera, Rep. Prog. Phys. 71, 016501 (2008).
20C. Noguera, J. Phys.: Condens. Matter 12, R367 (2000).
21D. Frenkel and B. Smit, Understanding Molecular Simulation, From Algorithms to Applications, 2nd ed. (Academic Press, San Diego, USA, 2002).
22M. P. Allen and D. J. Tildesley, Computer simulation of liquids, 2nd ed. (Oxford University Press, Oxford, UK, 2017).
23C. Zhang and M. Sprik, Phys. Rev. B 93, 144201 (2016).
24S. Spoehr, J. Chem. Phys. 107, 6342 (1997).
25L.-C. Yeh and A. Wallqvist, J. Chem. Phys. 134, 02B612 (2011).
26T. Croteau, A. Bertram, and G. Patey, J. Phys. Chem. A 113, 7826 (2009).
27B. Glatz and S. Sarupria, J. Chem. Phys. 145, 211924 (2016).
28S. A. Zielke, A. K. Bertram, and G. Patey, J. Phys. Chem. B 120, 2291 (2016).
29B. Glatz and S. Sarupria, Langmuir 34, 1190 (2017).
30Y. Ren, A. K. Bertram, and G. N. Patey, J. Phys. Chem. B 124, 4605 (2020).
31G. Roudsari, B. Reischl, O. H. Pakarinen, and H. Vehkamäki, J. Phys. Chem. C 124, 436 (2019).
32C. Zhang, J. Hutter, and M. Sprik, J. Phys. Chem. Lett. 10, 3871 (2019).
33C. Zhang, J. Chem. Phys. 149, 031103 (2018).
34C. Zhang, J. Hutter, and M. Sprik, J. Phys. Chem. Lett. 7, 2696 (2016).
35C. Zhang, J. Chem. Phys. 148, 156101 (2018).
36C. Zhang and M. Sprik, Phys. Chem. Chem. Phys. 22, 10676 (2020).
37J. C. Cox, Proc. Natl. Acad. Sci. USA 117, 19746 (2020).
38D. Pache and R. Schmid, ChemElectroChem 5, 1444 (2018).
39S. J. Cox and M. Sprik, J. Chem. Phys. 151, 064506 (2019).
40T. Dufils, G. Jeanmairet, B. Rotenberg, M. Sprik, and M. Salanne, Phys. Rev. Lett. 123, 195501 (2019).
41M. Sprik, Mol. Phys. 116, 3114 (2018).
42C. Zhang, T. Sayer, J. Hutter, and M. Sprik, J. Phys.: Energy 2, 032005 (2020).
43C. Pan, S. Yi, and Z. Hu, Phys. Chem. Chem. Phys. 21, 14858 (2019).
44For the wurtzite crystal structure of AgI studied in Ref. 15, more rapid convergence with n is seen than for the rocksalt structure.
45S. J. Cox, Z. Raza, S. M. Kethmann, B. Slater, and A. Michaelides, Faraday Discuss. 167, 389 (2013).
46G. C. Sosso, G. A. Tribello, A. Zen, P. Pedevilla, and A. Michaelides, J. Chem. Phys. 145, 211927 (2016).
47S. A. Zielke, A. K. Bertram, and G. Patey, J. Phys. Chem. B 120, 1726 (2015).
48S. J. Cox, D. J. Taylor, T. G. Youngs, A. K. Soper, T. S. Totton, R. G. Chapman, M. Arjmandi, M. G. Hodges, N. T. Skipper, and A. Michaelides, J. Am. Chem. Soc. 140, 3277 (2018).
49F. Vasconcelos, B. A. Bunker, and R. T. Cygan, J. Phys. Chem. C 111, 6753 (2007).
50C. M. Tenney and R. T. Cygan, Environ. Sci. Technol. 48, 2035 (2014).
51R. T. Cygan, J.-J. Liang, and A. G. Kalinichev, J. Phys. Chem. B 108, 1255 (2004).
52S. J. Soung and T. E. Cheatham III, J. Phys. Chem. B 112, 9020 (2008).
53P. Wirnsberger, D. Fijan, A. Šarić, M. Neumann, C. Dellago, and D. Frenkel, J. Chem. Phys. 144, 224102 (2016).
54H. Jiang, S. V. Levchenko, and A. M. Rappe, Phys. Rev. Lett. 108, 164603 (2012).
55L. Price, Faraday Discuss. 211, 9 (2018).
56J. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, J. Phys. Chem. 91, 6269 (1987).
57H. C. Andersen, J. Comput. Phys. 52, 24 (1983).
58W. Shinoda, M. Shiga, and M. Mikami, Phys. Rev. B 69, 134103 (2004).
59M. E. Tuckerman, J. Alejandre, R. López-Rendón, A. L. Jochim, and G. J. Martyna, J. Phys. A 39, 5629 (2006).
60R. W. Hockney and J. W. Eastwood, Computer simulation using particles (CRC Press, 1988).
61J. Kolafa and J. W. Perram, Mol. Sim. 9, 351 (1992).
62 S. Plimpton, J. Comput. Phys. 117, 1 (1995).
63 B. Hess, C. Kutzner, D. Van Der Spoel, and E. Lindahl, J. Chem. Theory Comput. 4, 435 (2008).
FIG. S1. Number density profiles $\rho$ of Na$^+$ and Cl$^-$ for kaolinite (0 0 0 1) in contact with aqueous electrolyte solution, in a mirrored slab geometry. (a) and (b) focus on the slabs at $z = -z_m$ and $z = +z_m$, respectively. The blue arrows indicates the orientation of the crystal [see Fig. 3 (a)]. These results agree well with those at $D = 0$ [see Fig. 3 (b)]. Simulation settings were the same as described in the main text, with $L = 15.0$ nm. We find $\sigma_x^{(\text{sim})} \approx 0.00$ e/nm$^2$. 
RESULTS FROM GROMACS

We have also performed simulations of the rocksalt (1 1 1) system using the GROMACS 4 simulation package. Simulation settings are broadly similar to those described in the main text, and specific details can be found in Refs. 13 and 14. For the mirrored slab geometry (Na⁺ exposed) a 3 nm vacuum gap was employed. All simulations were at least 2 ns long. Results are presented in Fig. S2, and are in excellent agreement with those obtained with LAMMPS (see Fig. 2). It is worth noting that the implementation of \( H_D \) in GROMACS was performed independently (see Ref. 23) from the implementation in LAMMPS (see Refs. 39 and 15).

![Figure S2](image-url)

**FIG. S2.** Results for the rocksalt (1 1 1) system obtained with GROMACS. These are in excellent agreement with results obtained with LAMMPS (see Fig. 2).