

Differential Capacitance of Electric Double Layers: A Poisson-Bikerman Formula

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Abstract. We propose a Poisson-Bikerman (PBik) formula for calculating the differential capacitance (DC) of electrical double layers (EDLs) in aqueous electrolytes or ionic liquids. The PBik theory is a generalization of the classical Poisson-Boltzmann theory to include different steric energies of different-sized ions and water similar to different electrical energies for different-charged ions. Water and ions with interstitial voids in this molecular mean field theory have their physical volumes as they do in molecular dynamics simulations. The PBik formula derived from Fermi distributions of ions and water in arbitrary shape and volume reduces to the Bikerman-Freise formula derived from the lattice model of equal-sized ions. The DC curves predicted by the Gouy-Chapman formula are U-shaped (for point-like ions with zero volume and very dilute solutions). The curves change from U shape to camel shape (Bactrian) and then to bell shape (for finite size ions) as the volume fraction of ions and water changes from zero to medium value then to large value. The transition is characterized

by critical and inflection voltages in terms of the particle volume fraction. These voltages determine steric and electrical energies that describe the space/charge competition and saturation properties of ions and water packed in the condensed layer of EDLs under high field conditions. Steric energy is as important as electrical energy in these conditions. PBik computes symmetric DC curves from delicately balanced steric interactions of asymmetric-size ions and water like the experimental data of KPF₆ in aqueous solution. It computes asymmetric curves and captures delicately balanced steric or electrical interactions of ions having different volumes or charges in ionic liquids.

1. INTRODUCTION

Differential capacitance (DC) measures the voltage-dependent capacitance of electrolyte capacitors [1]. It reflects the screening strength of electrical double layers (EDLs) that change with the surface potential of electrodes and the composition, concentration, charge, and size of ions and solvents that screen the potential in a complex way. The EDL determines most of the properties of solutions because of the enormous strength of the electric field compared to concentration fields, except in the most crowded situations. Studies of EDLs are of fundamental importance in adsorbent, energy, and membrane technologies [2–20] as well as in biological systems [21–29].

Classical theories of EDLs developed by Gouy and Chapman in the 1910s are based on the Poisson-Boltzmann (PB) equation, where ions are treated as point charges without volumes with distributions described by Boltzmann statistics [6, 8, 29]. These theories predict values of capacitance that diverge to infinity as the surface potential tends to infinity [8]. The divergence is not found experimentally and so it is not surprising that many authors have modified the Gouy-Chapman theory since Stern [30] in 1924. Ions are not points so it is natural to seek a remedy to divergence by including ionic volumes [2, 6, 8, 12, 19, 29]. Almost all these modified models (including those developed in recent years [3, 5, 6, 8, 9]) start with a lattice model of equal-sized ions proposed by Grimley and Mott [31] in 1947. This is unfortunate in our view. The assumption of equal size seems to us to produce degenerate models, because so few ions have equal volume. Unequal size must be expected to produce layering, as a glance at the relative size of say Na and Rb shows, and so would have behavior very different from the equal size case. It seems obvious that ions of different size must be

considered if the theory is to be used for biological or electrochemical systems, and indeed to have reasonably general validity, because all the solutions of biological interest and almost all of electrochemical interest include ions of quite different size. The unequal-sized model by Bikerman [32] in 1942 seems a much more reasonable place to start. We refer to recent reviews [6, 8, 12, 19, 29] of PB and modified PB models for comprehensive surveys and discussions of this topic.

To our knowledge, formulas are absent for the differential capacitance of solutions with any number of particle species with arbitrary shapes, volumes, and interstitial voids. We propose here such a formula derived from the Poisson-Bikerman (-Fermi) theory that yields (a) different steric energies for different-sized ions and molecular water and (b) different electrical energies for different-charged ions [29, 33]. In this molecular mean field theory, water and ions have their volumes as they do in molecular dynamics simulations. Distributions of these particles (ions and water molecules) are of Fermi type [6], i.e., ions saturate at large or even infinite potentials [29, 33].

The correlations produced by the interactions of steric and electrostatic potentials are well described in this theory over a range of conditions and length scales, or fits would not be possible [29]. We point out that higher resolution models (such as in all atom simulations) do not necessarily capture correlations as well as, let alone better than a mean field theory. The higher resolution models must actually be shown to capture correlations correctly in calibrated simulations; it is not obvious that simulations using periodic boundary conditions and lacking realistic boundary conditions can capture the correlations produced by the electric field. The electric field must be described by a continuum model because Maxwell's version of Ampere's law must include a time-varying electric field that is *not* associated with mass, and in fact extends into a vacuum reaching to the stars, if not infinity. Boundary conditions must be specified saying how the electric and magnetic fields connect to the outside world, or infinity. Thus the electric field cannot be described without boundary conditions. It cannot be computed without boundary conditions because mathematically speaking it does not exist without boundary conditions.

The Poisson-Bikerman (PBik) formula is analytical and semi-analytical for equal-sized and unequal-sized particles, respectively. Steric energies of different-sized ions and water molecules are analyzed with consistent mathematical models, consistently for both continuum and molecular models. Steric energies are important in dealing with mass conservation,

dehydration, dielectric, energetic, and selectivity properties. Indeed, steric energies are the main controllers of function in the crucially important calcium channels, transporters, and probably in the enzymes that control most biological systems. Steric energy controls function in the same sense that a gas pedal controls the speed of a car in these systems [34–40]. We show here the delicate effects of steric properties of ions and water on differential capacitance. Tiny changes in steric properties produce large changes in differential capacitance, or to say the same thing another way, measurements of differential capacitance can be used to determine the steric potential in some detail, as it changes with composition, concentration, and potential.

Bazant and co-workers [5, 8] and Kornyshev [6] revitalized the Bikerman-Freise [41] formula [8] which shows how DC curves change from U shape (predicted by the Gouy-Chapman formula for very dilute solutions or point-like ions at any concentration) to camel shape (Bac-trian) and then to bell shape (for realistic finite size ions). They introduced a mean volume fraction of ions to characterize the steric effects of uniform ions and use it to derive a critical (diffuse-layer) potential and explain the transition mechanism of these DC shapes [5]. The mean volume fraction is the product of the size and the bulk concentration of ions. We generalize the mean volume fraction to ions and water having nonuniform volumes and arbitrary shapes, where the volumes are physical.

The critical potential approximately separates monotonic and non-monotonic DC curves as the voltage varies from small to large [5, 8]. The critical potential can also be a voltage at a hypothetical interface between condensed and diffuse layers of electrical double layers at large voltage [5, 8]. We use our DC formula to define critical and inflection voltages, where a DC curve attains its extrema and inflection points (at which the curvature changes its sign), respectively. These voltages give a precise description of the transitions between condensed and diffuse layers, on the one hand, and monotonic and non-monotonic DC curves on the other.

The DC formula shows that the symmetric DC curves of experimental data of KPF₆ aqueous solution observed by Valette [42] arise from delicately balanced steric interactions of asymmetric-size ions and water. Asymmetric curves of ionic liquids result from asymmetric ions in size or charge, and the transitions of DC curves are characterized by the general mean volume fraction with its critical and inflection voltages.

2. THEORY

The total volume of an aqueous electrolyte system with K species of ions in a solvent domain Ω is

$$V = \sum_{i=1}^{K+1} v_i N_i + V_{K+2}, \quad (1)$$

where $K+1$ and $K+2$ denote water and voids, respectively, v_i is the volume of each species i particle, N_i is the total number of species i particles, and V_{K+2} is the total volume of all the voids [36]. Dividing this volume equation in bulk conditions by V , we get the bulk volume fraction of voids

$$\Gamma^b = 1 - \sum_{i=1}^{K+1} v_i c_i^b = \frac{V_{K+2}}{V}, \quad (2)$$

where $c_i^b = \frac{N_i}{V}$ are bulk concentrations. If the system is spatially inhomogeneous with variable electric or steric fields, as in realistic systems, the constants c_i^b then change to functions $c_i(\mathbf{r})$ for all \mathbf{r} in Ω and so does Γ^b to a function of void fractions

$$\Gamma(\mathbf{r}) = 1 - \sum_{i=1}^{K+1} v_i c_i(\mathbf{r}). \quad (3)$$

We define the concentrations (distributions) of ions and water in Ω as [33]

$$c_i(\mathbf{r}) = c_i^b \exp\left(-\beta_i \phi(\mathbf{r}) + \frac{v_i}{\bar{v}} S(\mathbf{r})\right), \quad S(\mathbf{r}) = \ln\left(\frac{\Gamma(\mathbf{r})}{\Gamma^b}\right), \quad (4)$$

for all $i = 1, \dots, K+1$, where $\phi(\mathbf{r})$ is an electrical potential, $S(\mathbf{r})$ is called a steric potential [33], $\beta_i = q_i/k_B T$ with q_i being the charge on species i ions, $q_{K+1} = 0$ for water, k_B is the Boltzmann constant, T is an absolute temperature, and $\bar{v} = \sum_{i=1}^{K+1} v_i / (K+1)$ is an average volume.

These distributions are of Fermi type (see Appendix A). The steric potential $S(\mathbf{r})$ depends on $\phi(\mathbf{r})$ and is an entropic measure of crowding or emptiness of particles at \mathbf{r} . If $\phi(\mathbf{r}) = 0$ and $c_i(\mathbf{r}) = c_i^b$ then $S(\mathbf{r}) = 0$. The factor v_i/\bar{v} shows that the steric energy $\frac{-v_i}{\bar{v}} S(\mathbf{r}) k_B T$ of a type i particle at \mathbf{r} depends not only on $S(\mathbf{r})$ but also on its volume v_i similar to the electrical energy $\beta_i \phi(\mathbf{r}) k_B T$ depending on both $\phi(\mathbf{r})$ and q_i [33]. The charge density $\rho(\mathbf{r}) = \sum_{i=1}^K q_i c_i(\mathbf{r})$ now includes different-sized ions as first proposed by Bikerman [32]. We extend his work in the following ways. We (a) introduce water as a molecule, (b) introduce the factor v_i/\bar{v} , (c) introduce the steric potential, and (d) prove the Fermi distribution. We

thus call the resulting equation

$$-\epsilon \nabla^2 \phi(x) = \rho(x), \quad x \in \Omega \quad (5)$$

a Poisson-Bikerman equation [29] in contrast to the classical Poisson-Boltzmann equation. Different names are needed because these two equations yield very different distributions (Appendix A). Here, $\epsilon = \epsilon_w \epsilon_0$ with ϵ_w being a dielectric constant (taken as 78.4 at room temperature) of water and ϵ_0 the vacuum permittivity.

To derive the differential capacitance formulas, we consider the domain Ω as a half real line. Eq 5 is then a 1D equation with $\mathbf{r} = x \in [0, \infty)$ and two boundary conditions $-\epsilon \frac{d\phi}{dx} \Big|_{x=0} = \sigma$ and $\phi(\infty) = 0$, where σ is a surface charge density. The differential capacitance of EDLs is

$$C_{v_i} = \epsilon \frac{d}{d\phi_0} \left\{ - \frac{d\phi}{dx} \Big|_{x=0} \right\}, \quad (6)$$

where $\phi_0 = \phi(0)$ is the surface potential, the subscript v_i indicates that ϕ depends on v_i in eq 5, and C_{v_i} is thus highly nonlinear in $\phi(x)$, $S(x)$, and v_i . It is very difficult, if not impossible, to derive an analytical formula for C_{v_i} . We can derive (Appendix B) the analytical DC formula

$$C_{\bar{v}}(\phi_0) = \frac{\pm \bar{C} \sum_{i=1}^K q_i c_i^b \exp(-\beta_i \phi_0)}{\exp(-S_0) \cdot \sqrt{-S_0}} \quad (7)$$

only for a special case of equal-sized ions and water, i.e., $v_i = \bar{v}, i = 1, \dots, K + 1$, where $\pm = \mp \text{sgn}(\sigma)$, $\bar{C} = \sqrt{\frac{\epsilon \bar{v}}{2k_B T}}$, $S_0 = S(\phi(0))$, and eq 3 simplifies to

$$1 = \exp(S) \left[\Gamma^b + \sum_{i=1}^{K+1} v_i c_i^b \exp(-\beta_i \phi) \right]. \quad (8)$$

The equal size assumption of particles ($\frac{v_i}{\bar{v}} = 1$) is the key to obtaining the formula 7 using eq 8 (Appendix B). The assumption yields the steric potential S_0 , a critical term in eq 7, that separates from ϕ_0 in eq 8. For different-sized particles ($\frac{v_i}{\bar{v}} \neq 1$), eq 8 becomes

$$1 = \exp(S) \left[\Gamma^b + \sum_{i=1}^{K+1} v_i c_i^b \exp \left(-\beta_i \phi + \left(\frac{v_i}{\bar{v}} - 1 \right) S \right) \right]. \quad (9)$$

We could not derive a formula from this equation like eq 7 because S cannot separate from ϕ in the exponential term when sizes are unequal. The steric potential S is a function of ϕ , namely, $S(\phi)$. Eq 8 yields an explicit (known) function $S(\phi) = -\ln \left[\Gamma^b + \sum_{i=1}^{K+1} v_i c_i^b \exp(-\beta_i \phi) \right]$ whereas eq 9 does not, i.e., $S(\phi)$ and ϕ mingle together

in a nonlinear (exponential) way via the volume term $\frac{v_i}{v} - 1$. It is not surprising that unequal sizes require a special treatment. A glance at the distribution of ionic charge that can occur if ions have opposite charges and very different sizes suggests that the reversal in the sign of the potential should be possible, because reversal in the *net* charge density is clearly possible [43]. Such disparate behavior is difficult to capture in an explicit algebraic formula.

We propose an empirical version of eq 7 as

$$C_{v_i}(\phi_0) = \frac{\pm \bar{C} \sum_{i=1}^K q_i c_i^b \exp(-\beta_i \phi_0 + \hat{S})}{\exp(-S_0) \sqrt{-S_0}}, \quad (10)$$

which is not analytical but semi-analytical from eq 7 by adding $\hat{S} := \hat{S}(\phi_0)$, an unknown (implicit) function of ϕ_0 to be determined by experimental data (Appendix C). Other perhaps better empirical expressions may be possible, although they are unknown to us. The differential capacitance $C_{v_i}(\phi_0)$ is thus exponentially sensitive to nonuniform v_i because $\hat{S}(\phi_0) \approx (\frac{v_i}{v} - 1)S(\phi_0)$.

It is important to check that the general differential capacitance formula 10 that we use reduces to known forms in appropriate special cases. (i) Formula 10 reduces to eq 7 obviously if $\frac{v_i}{v} = 1$ and $\hat{S} = 0$. (ii) It reduces to the Bikerman-Freise formula [5, 6, 8, 41] in Appendix D if $K = 2$, $q_1 = -q_2 = e$ (the elementary charge), and $v_1 = v_2 \neq 0$ (1:1 ionic liquids with equal-sized ions without water). (iii) It reduces to the Gouy-Chapman formula if $v_1 = v_2 = 0$ (point charges) [6]. (iv) It reduces to the Debye capacitance if $\phi_0 = 0$ in addition to those in (iii) [6].

Kornyshev introduced a mean volume fraction $\gamma = \bar{N}/N$ in his Poisson-Fermi theory of ionic liquids based on the lattice-gas model [6], where $\bar{N} = N_1 + N_2$ is the total number of cations N_1 and anions N_2 in the bulk of a binary ionic liquid and N is the total number of uniform lattice sites. We show in Appendix D that the general distribution model in eq 1 reduces to Kornyshev's uniform lattice model as a special case. Equivalently, the mean volume fraction γ is a special case of the sum of particle volume fractions $\tilde{\gamma} = \sum_{i=1}^{K+1} v_i N_i / V = \sum_{i=1}^{K+1} v_i c_i^b$, i.e.,

$$\tilde{\gamma} = \frac{v(N_1 + N_2)}{(vN)} = \frac{\bar{N}}{N} = 2vc^b = \gamma. \quad (11)$$

Eq 11 is in fact Bikerman's bulk ionic volume fraction (derived by Bazant and co-workers as well [5, 8]), where $v = 6\bar{v}/\pi$ is the volume of each site (assuming a primitive cubic lattice), $q_1 = -q_2 = e$, $v_1 = v_2 = v \neq 0$, and $c^b = c_1^b = c_2^b$.

In Appendix E, we obtain the inflection points (voltages)

$$|\phi_0^{**}| = -\alpha V_T \ln(\bar{v}c^b) \quad (12)$$

of $C_{\bar{v}}(\phi_0)$, i.e., $C_{\bar{v}}''(\phi_0^{**}) = 0$, where $V_T = k_B T/e$ is the thermal voltage and α is a factor of the diffuse-layer voltage [5, 8] $\phi_0^d = -V_T \ln(\bar{v}c^b)$ in $C_{\bar{v}}'(\phi_0^d) \approx C_{\bar{v}}'(\phi_0^*) = 0$. This factor is only a ratio of inflection ϕ_0^{**} and diffuse-layer ϕ_0^d voltages without physical meaning. The diffuse-layer ϕ_0^d (critical ϕ_0^*) voltage approximately (exactly) separates monotonic and non-monotonic DC curves as ϕ_0 varies from small to large [5, 8]. It is also a hypothetical voltage at the interface between condensed and diffuse layers of EDLs at large voltage [5, 8]. The inflection voltage ϕ_0^{**} is where a DC curve changes its curvature provided that $\bar{v}c^b \neq 0$ and $\bar{v}c^b \neq 1$.

Therefore, we further show the following. (v) The sum of volume fractions $\tilde{\gamma} = \sum_{i=1}^{K+1} v_i c_i^b$ is more general than the mean volume fraction $\gamma = 2vc^b$ in ref 5 and $\gamma = \bar{N}/N$ in ref 6 (Appendix D). It is more general because it includes ions and water having different volumes, arbitrary shapes, and any number of solution species.

(vi) From eq 12, if $\bar{v}c^b \rightarrow 0$ (point-like ions ($\bar{v} \rightarrow 0$) or infinite dilute solution ($c^b \rightarrow 0$)), then $\lim_{\bar{v} \rightarrow 0} |\phi_0^{**}| = \lim_{c^b \rightarrow 0} |\phi_0^{**}| = \infty$, i.e., the inflection voltages ϕ_0^{**} tend to $\pm\infty$ (they do not exist). The DC curve $C_{\bar{v}}(\phi_0)$ is therefore U-shaped for all ϕ_0 with only a unique minimum at $\phi_0^* = 0$ (Appendix E) as predicted by the Gouy-Chapman theory [5, 6].

(vii) If $0 < \bar{v}c^b < 1$, then $0 < |\phi_0^{**}| < \infty$, i.e., there are four finite inflection voltages $\pm\phi_0^{**} \neq 0$ and hence two more critical voltages $\pm\phi_0^* \neq 0$. It is mathematically impossible to have $\bar{v}c^b = 1$, the volume \bar{v} completely filled by ions or water molecules without voids (Appendix A). Therefore, the DC curve has three critical points ($\phi_0^* < 0$, $\phi_0^* = 0$, $\phi_0^* > 0$) and four inflection points (two for $\phi_0^{**} < 0$ and two for $\phi_0^{**} > 0$) and hence is camel-shaped. Furthermore, DC curves change from U shape in (vi) to camel shape [5, 6] as $\bar{v}c^b$ changes from zero to a medium number in the interval (0, 1).

(viii) If $\bar{v}c^b \rightarrow 1$, then $\lim_{\bar{v}c^b \rightarrow 1} |\phi_0^{**}| = 0 = \phi_0^*$. Again, the inflection voltages do not exist in this case because the limit value 0 is a critical voltage which yields a unique maximum of a DC curve (Appendix E). The curve is thus bell-shaped [5, 6]. DC curves hence change from camel shape in (vii) to bell shape as $\bar{v}c^b$ changes from the medium number to a larger number closer to one.

3. RESULTS

We first report PBik results by formula 10 for different sizes of ions and water to fit the experimental data of the differential capacitance $C_{v_i}(\phi_0)$ from Valette [42] for an electrochemical interface between a single-crystal Ag electrode (crystal plane (110)) and an aqueous KPF₆ electrolyte solution with negligible surface adsorption of ions. These results are particularly significant because they report the properties of an atomically clean surface in a defined plane of a perfect crystal structure. Measurements have been plagued for more than a century by surface contamination (the charge on the surface rapidly attracts charged ‘dirt’ in the solution). Different planes in a crystal obviously have different structures and charge distributions (in most cases) [42]. Thus they have different electrical properties and different EDLs. The plane must then be defined experimentally if results are to be reproducible, and that plane must be used in the corresponding theory.

The diameters of cation, anion, and water we use are $d_+ = 2.66$, $d_- = 4.69$, and $d_w = 2.8$ Å [42, 44], respectively. The potential shift at the interface is -0.97 V [16, 42] so we define $\bar{\phi}_0 = \phi_0 - 0.97$. Since the dielectric constant of various ionic liquids is about 15.5 on average [45], we use the permittivity function

$$\epsilon(\bar{\phi}_0) = \left[(78.4 - 15.5) \exp\left(-\frac{(\bar{\phi}_0 + 0.97)^2}{2 \cdot 0.1^2}\right) + 15.5 \right] \epsilon_0 \quad (13)$$

as a normal distribution of $\bar{\phi}_0$ with the mean value -0.97 V and the standard deviation 0.1 V at the experimental temperature 25 °C.

Figure 1 presents the PBik curves $C_{v_i}(\phi_0)$ from eq 10 using the spline method described in Appendix C fit to the experimental data (symbols) of aqueous KPF₆|Ag double layers. The bulk concentrations are 2.5, 10, 40, and 100 mM. These curves are nearly symmetrical about $\bar{\phi}_0 = 0.97$ ($\phi_0 = 0$) with respect to the surface potential $\bar{\phi}_0$ while the diameters of K⁺ ($v_+/\bar{v} = 0.39$ in eq 4) and PF₆⁻ ($v_-/\bar{v} = 2.15$) are very different. The steric interactions among K⁺, PF₆⁻, and water ($v_w/\bar{v} = 0.46$) play a significant role in the inner-layer capacity of ions in EDL [42]. The asymmetry (i.e., inequality) in size of K⁺, PF₆⁻, and water produces the asymmetry of the *empirical* steric potential \hat{S} (shown in Figure 2). On the other hand, the *analytical* steric potential S_0 profiles are nearly symmetrical (shown in Figure 3). The DC curves in $\bar{\phi}_0$ and also in S_0 are nearly symmetrical.

The steric energy at $\bar{\phi}_0 = -1.5$ V ($-\hat{S}_{K^+} k_B T$) in Figure 2 is larger than that at -0.5 V

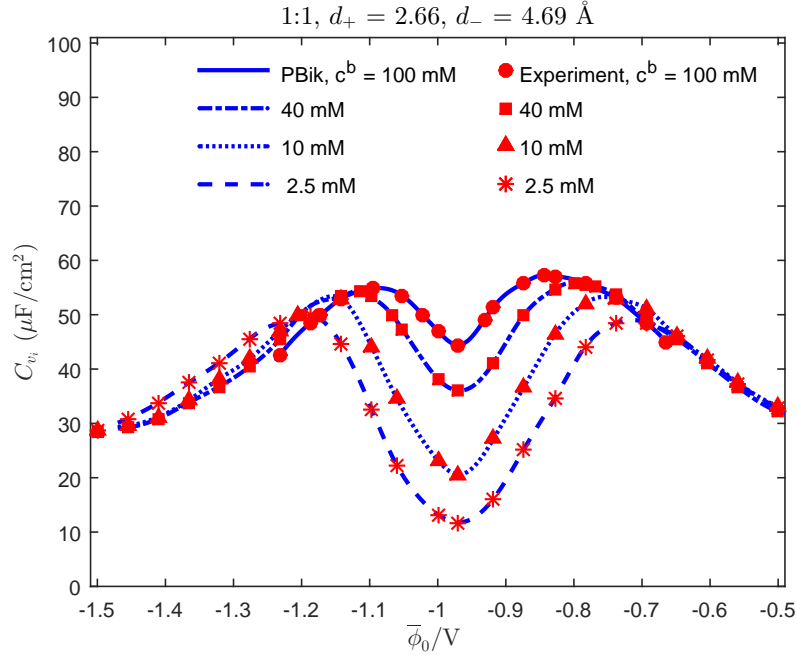


FIG. 1: PBik fitting curves by eq 10 to the DC experimental data [42] (symbols) of aqueous $\text{KPF}_6|\text{Ag}$ double layers at various concentrations.

$(-\hat{S}_{\text{PF}_6^-} k_B T)$, for example, because it is more crowded near the electrode for smaller K^+ ions at -1.5 V than for larger PF_6^- ions at -0.5 V. The effective width of the ‘EDL capacitor’ is larger for larger ions [5, 8]. Therefore, the change of $-\hat{S}_{\text{PF}_6^-} k_B T$ (the right wing in Figure 2) is larger than that of $-\hat{S}_{\text{K}^+} k_B T$ (the left wing) because of more room for rearranging of ions and water when the capacitance decreases from a global maximum in Figure 1 to lower values as the voltage varies (from small to large). \hat{S} also varies with the bulk concentration c^b of KPF_6 as shown in Figure 2.

Figure 4 shows that the symmetry of Figure 1 is broken when we slightly change the diameters from $d_+ = 2.66$ to $d_+ = 3$ and $d_- = 4.69$ to $d_- = 4$ Å. The same $\hat{S}(\phi_0)$ in formula 10 is used in both cases. The results show that $\hat{S}(\phi_0)$ is very sensitive to ionic diameter due to the factor $\frac{v_i}{v} - 1$ in eq 9. In this work, $\hat{S}(\phi_0)$ is empirical, strongly nonlinear in ϕ_0 , and highly sensitive to the sizes of ions and water. It also depends on the bulk concentrations of ions and water. It will be interesting to develop analytical $\hat{S}(\phi_0)$ in future studies.

We next present results using eq 7 for ionic liquids ($K = 2$) of equal-sized ions ($v_i = \bar{v}$) with the dielectric constant $\epsilon_{ion} = 10$ at $T = 25$ °C. The results demonstrate that the analytical formula 7 can successfully describe several important properties of differential

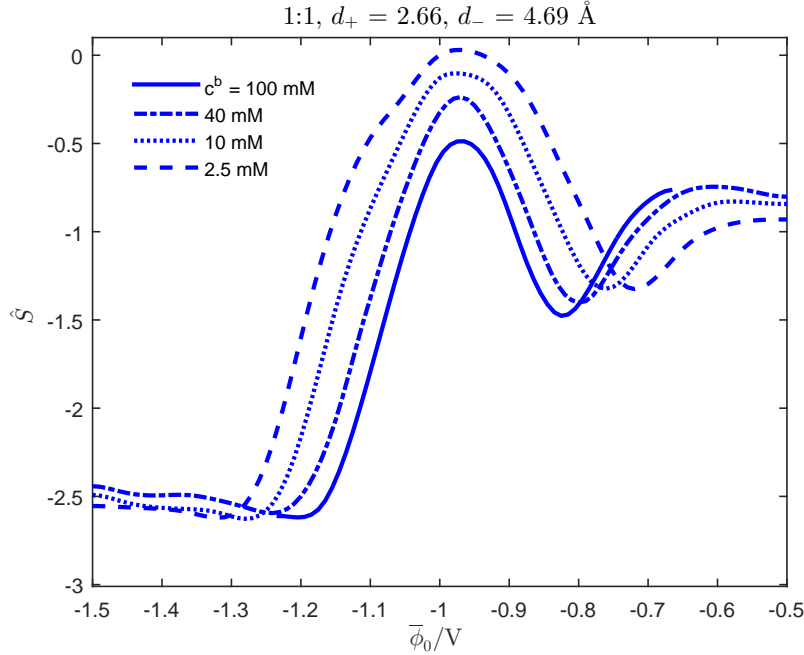


FIG. 2: Asymmetry of the steric energies $-\hat{S}k_B T \approx -\frac{v_i}{\bar{v}} S_0 k_B T$ of K^+ and PF_6^- in size (v_i) with respect to $\bar{\phi}_0$ about $\bar{\phi}_0 = -0.97$ V.

capacitance in electrical double layers. The success is possible because of the treatment of steric effects of molecules (including molecular water) within the mean-field framework.

Figure 5 shows two sets of DC curves $C_{\bar{v}}(\phi_0)$ for 1:1 ionic liquids with (a) $c^b = 0.01, 0.05, 0.1, 0.5, 1, 2$ M at fixed $d_{\pm} = 8$ Å and (b) $d_{\pm} = 2, 4, 6, 8, 14, 20$ Å at fixed $c^b = 0.02$ M, where the capacitance $C_{\bar{v}}$ is scaled by the Debye capacitance C_D and the surface potential ϕ_0 scaled by V_T . Figures 5a and 5b clearly demonstrate the transitions of DC curves $C_{\bar{v}}(\phi_0)$ from bell shape (with large c^b and d_{\pm} , respectively) to camel shape (medium c^b and d_{\pm}) then to U shape (small c^b and d_{\pm}) as predicted by eq 12.

Figure 6 illustrates the main properties of our theory by showing three curves of the first derivative $C'_{\bar{v}}(\phi_0)$ (Appendix E) for a 1:1 ionic liquid with $\bar{v}c^b =$ (a) 0.323, (b) 0.0161, and (c) 0.0016. Curves a, b, and c correspond to Curves 1, 2, and 3 in Figure 5a. Curve 1 is bell-shaped because $\bar{v}c^b = 0.323$ is large for large ions \bar{v} or large concentration c^b as shown in Point (viii) above. Curves 2 and 3 are camel and U-shaped because $\bar{v}c^b = 0.0161$ and $\bar{v}c^b = 0.0016$ are medium and small as shown in Points (vii) and (vi), respectively.

Curves a, b, and c show three sets of reflection voltages (ϕ_0^{**}) $\{1.38\}$, $\{2.87, 6.82\}$, and $\{5.14, 9.19\}$ (marked by circles), which yield $\{1.22\}$, $\{0.69, 1.65\}$, and $\{0.8, 1.43\}$ for α in

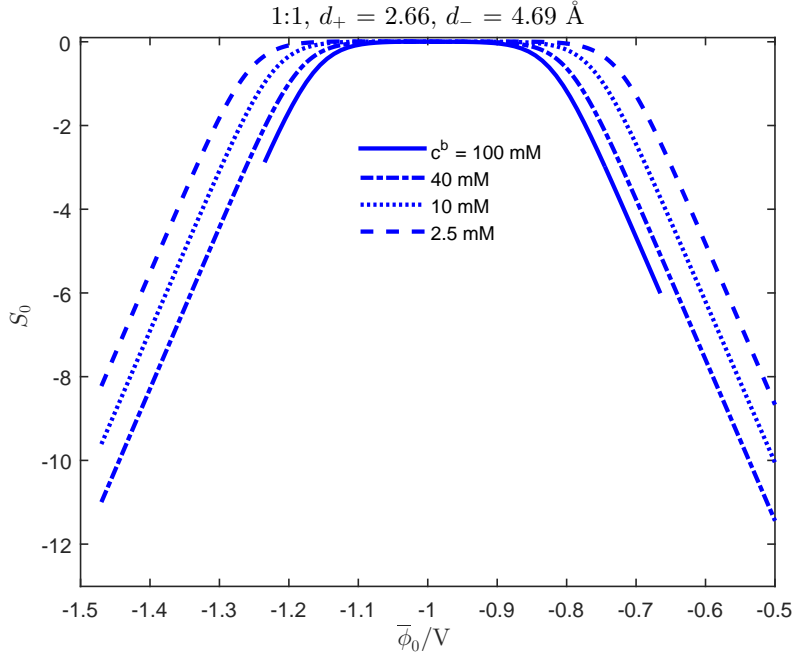


FIG. 3: Symmetry of the steric potential S_0 of aqueous $\text{KPF}_6|\text{Ag}$ double layers.

eq 12, respectively. The critical voltages (ϕ_0^*) are 0, 4.95, and 7.34 (squares). Voltages are all in V_T . For Curve b (Curve 2 in Figure 5a), for example, $\phi_0^* = 0, 4.95$; $\phi_0^{**} = 2.87, 6.82$; and $\alpha = 0.69, 1.65$. The ionic liquid with $\bar{v}c^b = 0.0161$ attains its maximal capacitance at $\phi_0^* = 4.95 \approx \phi_0^d = -\ln(\bar{v}c^b) = 4.13$.

The critical voltage $\phi_0^* = 4.95$ determines a critical steric potential S_0^* of the ionic liquid that yields the maximal capacitance

$$C_{\bar{v}}^{\max}(\phi_0^*) = \frac{ec^b\bar{C}[\exp(\phi_0^*/V_T) - \exp(-\phi_0^*/V_T)]}{\exp(-S_0^*)\sqrt{-S_0^*}} = 2.5C_D \quad (14)$$

shown in Figure 5a and produces a condensed layer [5, 8] of ions packed along the electrode due to the excluded volume \bar{v} . When ϕ_0 increases from ϕ_0^* to larger values ($\phi_0 > 4.95$), the capacitance $C_{\bar{v}}(\phi_0)$ decreases from $C_{\bar{v}}^{\max}(\phi_0^*)$, i.e.,

$$\frac{C_{\bar{v}}(\phi_0)}{C_{\bar{v}}^{\max}(\phi_0^*)} = \frac{[\exp(\phi_0/V_T) - \exp(-\phi_0/V_T)] \exp(-S_0) \sqrt{-S_0}}{[\exp(\phi_0^*/V_T) - \exp(-\phi_0^*/V_T)] \exp(-S_0^*) \sqrt{-S_0^*}} < 1, \quad (15)$$

$$\frac{\exp(\phi_0/V_T) - \exp(-\phi_0/V_T)}{\exp(\phi_0^*/V_T) - \exp(-\phi_0^*/V_T)} < \frac{\exp(-S_0) \sqrt{-S_0}}{\exp(-S_0^*) \sqrt{-S_0^*}}.$$

Both sides of the inequality 15 are positive and increasing with ϕ_0 . The inequality hence shows that the steric potential S_0 (crowding energies) becomes more dominant than the

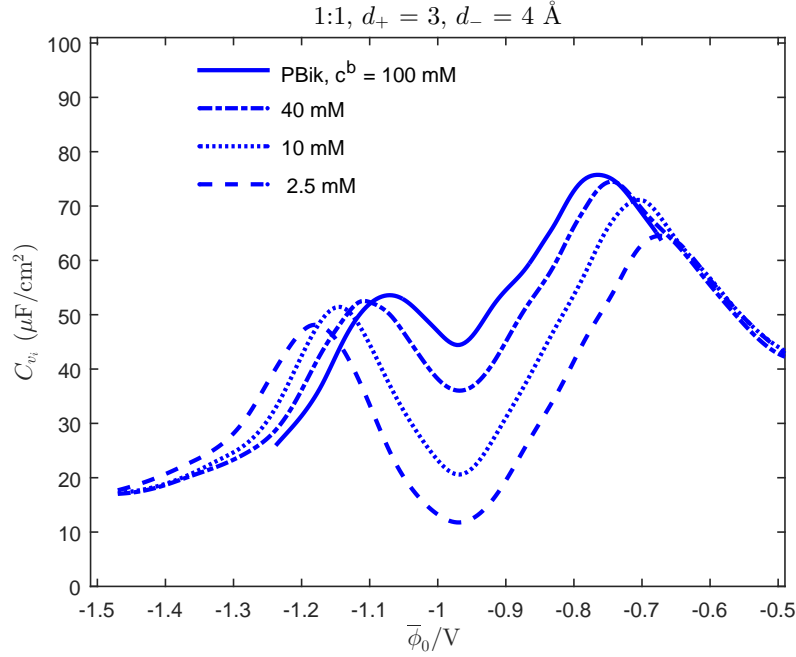


FIG. 4: Broken symmetry of Figure 1 by slight changes of the diameters d_{\pm} .

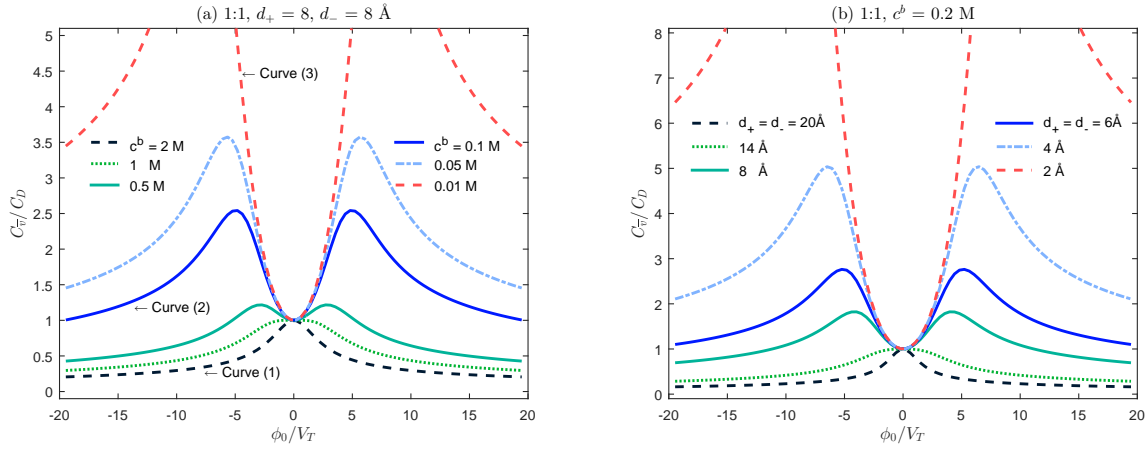


FIG. 5: Transition of DC curves $C_{\bar{v}}(\phi_0)$ for 1:1 ionic liquids by eq 12 from bell shape (Curve 1, for example) with large (a) c^b and (b) d_{\pm} to camel shape (Curve 2) with medium c^b and d_{\pm} then to U (Curve 3) shape with small c^b and d_{\pm} .

electrical potential ϕ_0 (charging energies) when the surface potential ϕ_0 is greater than the critical voltage ϕ_0^* . This implies that the concentration

$$c_-(\phi_0) = c_-^b \exp(-\beta_- \phi_0 + S_0) \quad (16)$$

of packed ions (anions) decreases with ϕ_0 because S_0 is more negative yielding larger steric

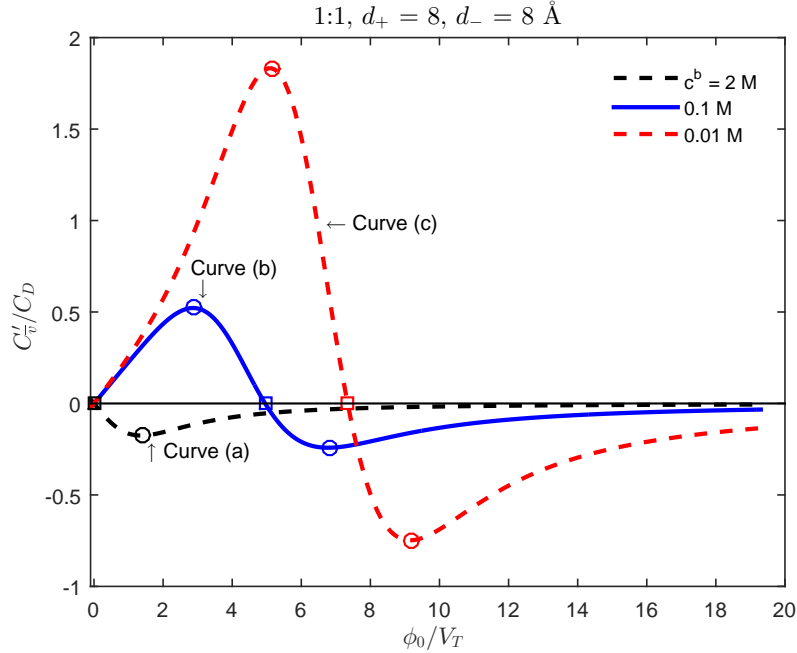


FIG. 6: Critical (squares) and inflection (circles) voltages determined approximately, i.e., $C'_v(\phi_0^*) = 0$ and $C''_v(\phi_0^{**}) = 0$, respectively, by the curves of $C'_v(\phi_0)/C_D$ with $\bar{v}c^b =$ (a) 0.323 (Curve 1 in Figure 5a), (b) 0.0161 (Curve 2), and (c) 0.0016 (Curve 3).

(positive) energies $-S_0k_B T$ for more anions to leave the packed region, i.e., the capacitance $C_{\bar{v}}(\phi_0)$ decreases with ϕ_0 as shown in Figure 5a.

The inflection voltage $\phi_0^{**} = 6.82$ describes the saturation property of the ionic liquid at even greater ϕ_0 because ions have physical volumes. The steric potential $S_0 = S(\phi_0)$ is non-positive and bounded, i.e., there exists $S_0^{\min} = \ln \frac{\Gamma_0^{\min}}{\Gamma^b}$ such that $S_0^{\min} \leq S_0 \leq 0$, $\Gamma_0^{\min} = 1 - \bar{v}c_-^{\max}$, and $c_-^{\max} < \frac{1}{\bar{v}}$ (Appendix A). From eq 16, we have

$$\lim_{\phi_0 \rightarrow \phi_0^{\max}} c_-(\phi_0) = c_-^b \exp(-\beta_- \phi_0^{\max} + S_0^{\min}) = c_-^{\max}, \quad (17)$$

a saturating concentration with the limits ϕ_0^{\max} and S_0^{\min} to which the electrical and steric potentials of the system cannot surpass. This implies that the DC curve $C_{\bar{v}}(\phi_0)$ approaches a flat line shown in Figure 5a as $\phi_0 \rightarrow \phi_0^{\max}$. The curve changes its curvature at $\phi_0^{**} = 6.82$ from concave down in $2.87 < \phi_0 < 6.82$ to concave up in $6.82 < \phi_0 \leq \phi_0^{\max}$ so anions can saturate at c_-^{\max} having balanced electrical ($\beta_- \phi_0^{\max} k_B T$) and steric ($-S_0^{\min} k_B T$) energies. The electrical and steric energies at $\phi_0 = 20V_T$ in Figure 5a are $-20k_B T$ and $15.87k_B T$, respectively. Steric energy is as important as electrical energy in this condition. These two

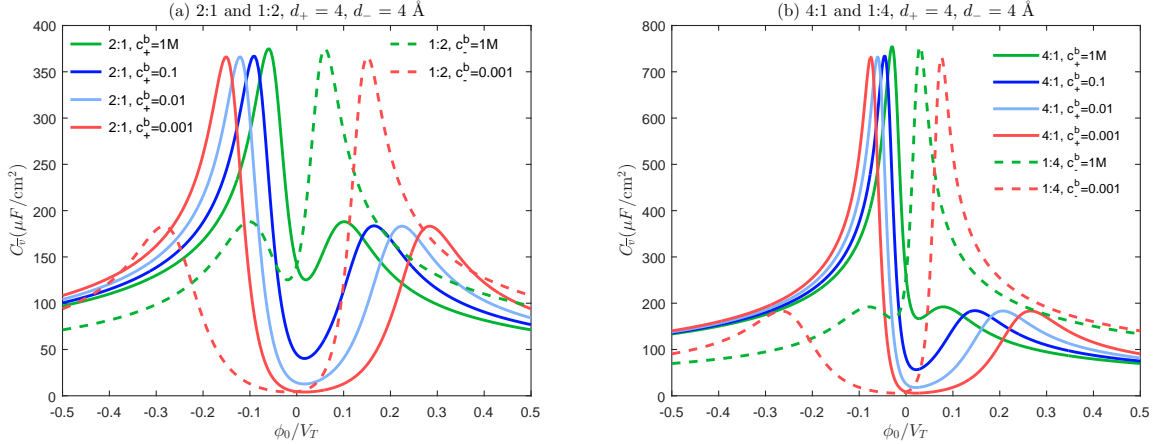


FIG. 7: Asymmetry of DC curves for charge-asymmetric ions in (a) 2:1, 1:2 and (b) 4:1, 1:4 ionic liquids at various concentrations and fixed $d_{\pm} = 4 \text{ \AA}$.

energies are in fact competing with each other in the high field (packed) region similar to the space/charge competition in the binding site of biological ion channels crowded with ions [29, 48–50].

Finally, Figure 7 shows that DC curves are asymmetric for ions with unequal charges in (a) 2:1, 1:2 and (b) 4:1, 1:4 ionic liquids at various concentrations and fixed $d_{\pm} = 4 \text{ \AA}$. The more the charge difference is between ions (4:1 vs 2:1 for example), the larger the difference is between global maximal and minimal capacitance (800 vs 400 for C_T in Figures 7b and 7a). The maximal capacitance doubles (800 vs 400) if the charge of ions doubles (4:1 vs 2:1). Comparing green and red curves in Figure 7a shows the underlying qualitative principle. The more the concentration of an ionic liquid is ($c_+^b = 1$ vs $c_+^b = 0.001$), the smaller the capacitance difference is and the narrower between two peaks of a curve (green vs red).

4. CONCLUSION

We propose and analyze the differential capacitance (DC) using a formula derived from the Poisson-Bikerman theory. The formula accounts for varying steric energies of ions and water in aqueous electrolytes and in ionic liquids (without water) with different sizes, charges, concentrations, and compositions. The formula reduces to its classical or contemporary counterpart when the steric energy vanishes or the ionic size is uniform, displaying the degenerate nature of models that assume equal diameters, or no volume at all, or no volume

for water molecules. The analysis shows that the differential capacitance of electrolytes near highly electrified interfaces is determined by the interplay between electrical and steric energies of ions and water.

The differential capacitance is characterized by critical and inflection voltages that are defined by a sum of particle volume fractions. It is important to note that the sum is more general than the mean volume fraction of equal-sized ions proposed in earlier work. The sum of particle volumes in the present paper includes *any* arbitrary species of ions and water with *any* shapes and volumes. The critical and inflection voltages describe the transition mechanism of DC curves changing from (i) bell shape (for large values of ionic size or concentration) to (ii) (double-humped Bactrian) camel shape (for medium value) and then to (iii) U shape (for small values). The critical voltage also shows that the steric energy of ions and water becomes more important than the electrical energy of ions in the adsorbed region of strongly electrified interfaces. The inflection voltage also describes the saturation property of ions and water in the adsorbed region as the applied voltage of the electrolyte system reaches to its physical maximum.

Numerical results illustrate the transition of shapes of DC curves and the symmetry of experimental DC data for aqueous KPF₆ electrolyte solution, which results from delicate interactions of asymmetric ions and water in size. The asymmetry of DC curves come from the unequal charge of ions of the same size; or it can come from the unequal size of ions of the same charge. The more the charge difference is between ions, the larger the difference is between global maximal and minimal capacitance.

5. APPENDICES

Appendix A. We show here the fundamental difference between classical Poisson-Boltzmann and present Poisson-Bikerman theories that yield Boltzmann and Fermi distributions of particles, respectively. Substituting eqs 2 and 3 into eq 4 and rearranging terms give

$$[c_i(\mathbf{r})]^{\bar{v}} = \frac{[c_i^b \exp(-\beta_i \phi(\mathbf{r}))]^{\bar{v}}}{(\Gamma^b)^{v_i}} \left(1 - \sum_{j \neq i}^{K+1} v_j c_j(\mathbf{r}) - v_i c_i \right)^{v_i}$$

$$[c_i(\mathbf{r})]^{\bar{v}/v_i} + \alpha_i v_i c_i(\mathbf{r}) = \alpha_i \left(1 - \sum_{j \neq i}^{K+1} v_j c_j(\mathbf{r}) \right),$$

where $\alpha_i = [c_i^b \exp(-\beta_i \phi(\mathbf{r}))]^{\bar{v}/v_i} / \Gamma^b$ for $i = 1, \dots, K + 1$. Define $f(t) = t^{\bar{v}/v_i} + \alpha_i v_i t$ which is an increasing function and satisfies

$$f(c_i(\mathbf{r})) = \alpha_i \left(1 - \sum_{j \neq i}^{K+1} v_j c_j(\mathbf{r}) \right) < \alpha_i = \alpha_i v_i \cdot (1/v_i) < f(1/v_i).$$

Therefore, $c_i(\mathbf{r})$ are bounded from above (Fermi distributions), i.e., $c_i(\mathbf{r})$ cannot exceed the maximum value $1/v_i$ for any arbitrary (or even infinite) potential ϕ at any location \mathbf{r} in the domain $\bar{\Omega}$.

In these mean-field Fermi distributions, it is impossible for a volume v_i to be completely filled with ions, i.e., it is impossible to have $v_i c_i(\mathbf{r}) = 1$ (and thus $\Gamma(\mathbf{r}) = 1 - v_i c_i(\mathbf{r}) = 0$) since that would make $S(\mathbf{r}) = \ln \frac{\Gamma(\mathbf{r})}{\Gamma^b} = -\infty$ and hence $c_i(\mathbf{r}) = 0$, a contradiction. Therefore, *we must include the void as if it were a separate species if we treat ions and water having volumes in a model.* This is a critical property distinguishing our theory from others that do not consider explicitly the steric potential $S(\mathbf{r})$ with the factor v_i/\bar{v} and the variable volume v_i [29]. The steric potential is consistent with the classical theory of van der Waals in molecular physics [29], which describes nonbond interactions between any pair of atoms as a distance-dependent potential such as the Lennard-Jones potential that cannot have zero distance between the pair [29].

In general, we have $\Gamma(\mathbf{r}) < \Gamma^b$ (or $S(\mathbf{r}) < 0$) when $\phi(\mathbf{r}) \neq 0$ since $c_i^b \exp(-\beta_i \phi(\mathbf{r})) > c_i^b$ for $-\beta_i \phi(\mathbf{r}) > 0$ meaning that negative (positive) $\phi(\mathbf{r})$ at \mathbf{r} attracts positive (negative) ions of type i to \mathbf{r} and yields $c_i(\mathbf{r}) > c_i^b$. We also obtain Boltzmann distributions that diverge if $-\beta_i \phi(\mathbf{r}) \rightarrow \infty$ at some \mathbf{r} for $\beta_i \neq 0$ (ions not water), i.e., $\lim_{-\beta_i \phi(\mathbf{r}) \rightarrow \infty} c_i^b \exp(-\beta_i \phi(\mathbf{r}) + \frac{v_i}{\bar{v}} S(\mathbf{r})) = \infty$ when $S(\mathbf{r}) = 0$, i.e., as $v_i \rightarrow 0$ for all $i = 1, \dots, K + 1$ (all ions and water are treated without volumes).

It is important to note that we discovered the importance of the ‘extra volume’ when we started treating water as a molecule with definite volume. We could not compute our model without including the extra volume [35]. When water was described in a primitive way as a uniform background dielectric, the computation was not so severely affected. It is possible that workers using the simple primitive model [28, 43, 51] of classical fluid theory may have been frustrated by similar unresolved problems.

Appendix B. We now derive eq 7 for equal-sized ions and water, which is a key formula in the present work and displays a novel and explicit relationship between electrostatic (the numerator term) and steric (denominator) potentials. From eqs 5 and 8 with a change of

variable $u = d\phi/dx$, we have

$$\begin{aligned} -\epsilon u du &= \rho d\phi = \sum_{i=1}^{K+1} q_i c_i^b \exp(-\beta_i \phi + S) d\phi \\ &= \exp(S) \sum_{i=1}^{K+1} q_i c_i^b \exp(-\beta_i \phi) d\phi \end{aligned} \quad (\text{B1})$$

$$= \frac{\sum_{i=1}^{K+1} q_i c_i^b \exp(-\beta_i \phi)}{\Gamma^b + \sum_{i=1}^{K+1} v_i c_i^b \exp(-\beta_i \phi)} d\phi \quad (\text{B2})$$

Introducing $w = \Gamma^b + \sum_{i=1}^{K+1} v_i c_i^b \exp(-\beta_i \phi)$ and using

$$\frac{dw}{d\phi} = \bar{v} \sum_{i=1}^{K+1} -\beta_i c_i^b \exp(-\beta_i \phi) \quad (\text{B3})$$

yield

$$\begin{aligned} -\int \epsilon u du &= \int \frac{\sum_{i=1}^{K+1} q_i c_i^b \exp(-\beta_i \phi)}{w} d\phi = \int \frac{-k_B T / \bar{v}}{w} dw \\ \frac{-\epsilon u^2}{2} &= \frac{-k_B T}{\bar{v}} \ln w + c, \end{aligned}$$

where $c = 0$ since $\phi(\infty) = 0$ implying that $w = 1$ and $u(\infty) = 0$, i.e., the electric field vanishes at ∞ . We thus have

$$u = \frac{d\phi}{dx} = \pm \sqrt{\frac{2k_B T}{\epsilon \bar{v}} \ln \left[\Gamma^b + \sum_{i=1}^{K+1} v_i c_i^b \exp(-\beta_i \phi) \right]}.$$

The boundary condition $-\epsilon \phi'(0) = -\epsilon u_0 = \sigma$ implies that $u_0 < 0$ if $\sigma > 0$ and $u_0 > 0$ if $\sigma < 0$ and hence $\pm = \mp \text{sign}(\sigma)$. We thus obtain the formula 7 by eq 6, eq 8, and

$$\begin{aligned} C_{\bar{v}} &= \mp \epsilon \frac{d}{d\phi_0} \left\{ \left(\frac{2k_B T}{\epsilon \bar{v}} \ln \left[\Gamma^b + \sum_{i=1}^{K+1} v_i c_i^b \exp(-\beta_i \phi_0) \right] \right)^{1/2} \right\} \\ &= \pm \epsilon \sqrt{\frac{k_B T}{2\epsilon \bar{v}}} \left(\ln \left[\Gamma^b + \sum_{i=1}^{K+1} v_i c_i^b \exp(-\beta_i \phi_0) \right] \right)^{-1/2} \\ &\quad \frac{\sum_{i=1}^{K+1} \beta_i v_i c_i^b \exp(-\beta_i \phi_0)}{\Gamma^b + \sum_{i=1}^{K+1} v_i c_i^b \exp(-\beta_i \phi_0)}. \end{aligned} \quad (\text{B4})$$

The equal size assumption of particles ($\frac{v_i}{\bar{v}} = 1$) is a key to derive eq 7 as shown in eqs B1, B2 by 8, B3, and B4 to 7 by 8.

Appendix C. The differential capacitance eq 10 is for any arbitrary species of ions and water with any shapes and volumes. The steric term \hat{S} in eq 10 is a nonlinear function of the surface potential ϕ_0 for which we cannot obtain an explicit formula.

We approximately determine \hat{S} by the following fitting method to the experimental data $C_{exp}(\phi_{0,k})$ of Valette [42]. Setting $C_{v_i}(\phi_{0,k}) = C_{exp}(\phi_{0,k})$ yields $\hat{S}_k := \hat{S}(\phi_{0,k})$, i.e., $n + 1$ values of \hat{S} at $\phi_{0,0} < \phi_{0,1} < \dots < \phi_{0,n} =: [a, b]$ for $k = 0, \dots, n$. We then use the cubic spline method to find a function $s(\phi_0)$ at these $n + 1$ interpolation points such that

$$s_k = \hat{S}_k, k = 0, \dots, n$$

$$s_{k-}^{(j)} = s_{k+}^{(j)}, k = 1, \dots, n - 1, j = 0, 1, 2,$$

where $s_k := s(\phi_{0,k})$ and $s_{k\pm}^{(j)}$ is the j^{th} derivative of $s(\phi_0)$ with respect to ϕ_0 at $\phi_{0,k\pm} := \lim_{\Delta\phi_0 \rightarrow 0} \phi_{0,k} \pm \Delta\phi_0$. Introducing the notation $M_k := s_k^{(2)} = s_{k\pm}^{(2)}$, the spline function

$$s(\phi_0) = \frac{(\phi_{0,k+1} - \phi_0)^3 M_k + (\phi_0 - \phi_{0,k})^3 M_{k+1}}{6h_k} + \frac{(\phi_{0,k+1} - \phi_0)\hat{S}_k + (\phi_0 - \phi_{0,k})\hat{S}_{k+1}}{h_k} - \frac{h_k}{6} [(\phi_{0,k+1} - \phi_0)M_k + (\phi_0 - \phi_{0,k})M_{k+1}]$$

and its second derivative $s^{(2)}(\phi_0)$ are continuous functions on the interval $[a, b]$, where $k = 0, 1, \dots, n - 1$, $\phi_0 \in [\phi_{0,k}, \phi_{0,k+1}]$, and $h_k = \phi_{0,k+1} - \phi_{0,k}$. To determine the unknown constants M_0, \dots, M_n , we impose $s^{(1)}(\phi_0)$ to be continuous in $[a, b]$ as well, i.e.,

$$\frac{h_{k-1}}{6} M_{k-1} + \frac{h_k + h_{k-1}}{3} M_k + \frac{h_k}{6} M_{k+1} = \frac{\hat{S}_{k+1} - \hat{S}_k}{h_k} - \frac{\hat{S}_k - \hat{S}_{k-1}}{h_{k-1}}$$

$$s_0^{(1)} = 0, s_n^{(1)} = 0.$$

for $k = 1, \dots, n - 1$.

Appendix D. This appendix shows that the DC formula 7 derived from eq 1 is more general than that from the uniform lattice model. The sum of particle volume fractions $\tilde{\gamma} = \sum_{i=1}^{K+1} v_i N_i / V = \sum_{i=1}^{K+1} v_i c_i^b$ for arbitrary species of ions and water with any shapes and volumes is also more general than the mean fraction formulas of Kornyshev ($\gamma = \bar{N}/N$) [6] and Kilic et al. ($\gamma = 2vc^b$) [5] with two species ions of the same size.

As a special case, formula 7 reduces to the Bikerman-Freise formula [8]

$$C_{BF} = \frac{C_D \cosh(\frac{\phi_0}{2V_T}) \sqrt{2\gamma \sinh^2(\frac{\phi_0}{2V_T})}}{(1 + 2\gamma \sinh^2(\frac{\phi_0}{2V_T})) \sqrt{\ln(1 + 2\gamma \sinh^2(\frac{\phi_0}{2V_T}))}}$$

also derived by Kornyshev (eq 20 in ref 6) and Kilic et al. [5] if we replace the mean fraction γ with

$$\tilde{\gamma} = \frac{(v_1 N_1 + v_2 N_2)}{V} = \frac{v(N_1 + N_2)}{(vN)} = \frac{\bar{N}}{N} = 2vc^b. \quad (D1)$$

Here $\bar{N} = N_1 + N_2$ is the total number of cations N_1 and anions N_2 in the bulk, N is the total number of uniform lattice sites [6], $v = 8 \cdot \frac{3\bar{v}}{4\pi}$ is the volume of each site (assuming a primitive cubic system), $K = 2$, $q_1 = -q_2 = e$, $v_1 = v_2 = v \neq 0$, $c^b = c_1^b = c_2^b$, and $C_D = \sqrt{\frac{2\epsilon\epsilon^2 c^b}{k_B T}}$ is the Debye capacitance. Note that $\tilde{\gamma} = \gamma$ and $\tilde{\gamma} < \gamma$ for two different volumes v and \bar{v} of two equal-sized ions occupying their sites without and with voids, respectively, because $v > \bar{v}$. We assume $v_1 = v_2 = v$ in the general $\tilde{\gamma}$ as that in the special γ .

Since probabilities have to sum up to 1, we have

$$\begin{aligned} 1 &= \Gamma + v(c_1 + c_2) \\ &= \exp(S)\Gamma^b + v c^b (e^{-\frac{\phi_0}{V_T}} + e^{\frac{\phi_0}{V_T}}) \exp(S) \\ &= \exp(S)(1 - 2v c^b + 2v c^b \cosh \frac{\phi_0}{V_T}). \end{aligned}$$

This yields the key relation

$$\exp(-S) = 1 - \gamma + \gamma \cosh\left(\frac{\phi_0}{V_T}\right) = 1 + 2\gamma \sinh^2 \frac{\phi_0}{2V_T}. \quad (\text{D2})$$

Thus,

$$\begin{aligned} C_v &= \frac{\pm \bar{C} \sum_{i=1}^2 q_i c_i^b \exp(-\beta_i \phi_0)}{\exp(-S_0) \cdot \sqrt{-S_0}} \\ &= \frac{\pm \sqrt{\frac{\epsilon v}{2k_B T}} \cdot e c^b (\exp(-\phi_0/V_T) - \exp(\phi_0/V_T))}{(1 + 2\gamma \sinh^2 \frac{\phi_0}{2V_T}) \sqrt{\ln(1 + 2\gamma \sinh^2 \frac{\phi_0}{2V_T})}} \\ &= \frac{\pm \sqrt{\frac{2\epsilon\epsilon^2 c^b}{k_B T}} \cdot \frac{\sqrt{v c^b}}{2} (\exp(-\phi_0/V_T) - \exp(\phi_0/V_T))}{(1 + 2\gamma \sinh^2 \frac{\phi_0}{2V_T}) \sqrt{\ln(1 + 2\gamma \sinh^2 \frac{\phi_0}{2V_T})}} \\ &= \frac{\mp C_D \sqrt{\gamma} \sinh\left(\frac{\phi_0}{V_T}\right)}{\sqrt{2}(1 + 2\gamma \sinh^2 \frac{\phi_0}{2V_T}) \sqrt{\ln(1 + 2\gamma \sinh^2 \frac{\phi_0}{2V_T})}}, \end{aligned}$$

and we have the desired result $C_v = C_{BF}$ and the Gouy-Chapman law $\lim_{v \rightarrow 0} C_v = C_{GC} = C_D \cosh\left(\frac{\phi_0}{2V_T}\right)$ [6].

Appendix E. Figure 6 illustrates three curves of the first derivative $C'_v(\phi_0)$ of the DC $C_{\bar{v}}(\phi_0)$ in eq 7 with respect to the surface potential ϕ_0 . Those curves yield critical (ϕ_0^*) and inflection (ϕ_0^{**}) voltages which describe the transition, space/charge competition, and saturation properties of ions and water in the condensed layer of EDLs. We explain how to obtain those curves and voltages.

Differentiating $C_{\bar{v}}(\phi_0)$ yields the numerator part

$$[-\beta_1 \exp(-\beta_1 \phi_0) + \beta_2 \exp(\beta_2 \phi_0)] \exp(-S_0) \sqrt{-S_0} - [\exp(-\beta_1 \phi_0) - \exp(\beta_2 \phi_0)] \left[\exp(-S_0) \sqrt{-S_0} + \frac{1}{2} (-S_0)^{-1/2} \exp(-S_0) \right] \frac{d(-S_0)}{d\phi_0}.$$

Setting this expression to zero and omitting all the intermediate algebra, we obtain the equation

$$-S_0 [(1 - 2\bar{v}c^b)(t + t^{-1}) + 4\bar{v}c^b] - \bar{v}c^b (t - t^{-1})^2 / 2 = 0$$

for finding critical voltages, i.e., $C'_{\bar{v}}(\phi_0^*) = 0$, where $t = \exp(-\beta_1 \phi_0)$. If $\phi_0 = 0$, then $1 = \exp(S_0) [\Gamma^b + 2\bar{v}c^b] = \exp(S_0)$ by eqs 2 and 8, $S_0 = 0$, and $C'_{\bar{v}}(0) = 0$. Therefore, the DC curve $C_{\bar{v}}(\phi_0)$ has a local minimum or maximum at $\phi_0^* = 0$. If $\bar{v} = 0$ as in the Gouy-Chapman theory, then $C_{\bar{v}}(\phi_0) = C_D \cosh(\frac{\phi_0}{2V_T})$ (Appendix D) is of U shape and has a global minimum at $\phi_0^* = 0$. If $0 < \bar{v}c^b < 1$, we can numerically draw the graph of $C'_{\bar{v}}(\phi_0)$ as shown in Figure 6, then get two inflection voltages $\pm\phi_0^{**}$, i.e., $C''_{\bar{v}}(\pm\phi_0^{**}) = 0$, and thus obtain the camel shape of DC curves as shown in Figures 5a and 5b. If $\bar{v}c^b \rightarrow 1$, then $\phi_0^{**} \rightarrow 0 = \phi_0^*$ by eq 12, i.e., the inflection voltage does not exist, $C'_{\bar{v}}(\phi_0)$ has only one root ϕ_0^* , and the curve is of bell shape as shown in Figure 5a for the case of $\bar{v}c^b = 0.323$ with $\bar{v} = \pi 4^4 / 3 \text{ \AA}^3$ and $c^b = 2 \text{ M} = 2 / (1660.6 \text{ \AA}^3)$, for example.

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