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Limitations and strengths of uniformly charged double-layer theory: Physical significance of capacitance anomalies

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Theoretical studies of electrical double layers typically consider the response of ionic conductors to the field of uniform charge-density distributions σ ("σ-control"). Many such analyses predict apparent anomalies of differential capacitance, C, including divergences and negative values. To clarify misconceptions regarding these predictions, we critically reexamine some theoretical approaches dealing with the admissible sign of C. We examine the anomalies' origin and stress its relation to the artificiality of σ-control. We show that calculations based on σ-control can illuminate the nature of instabilities and phase transitions under the physically attainable conditions of potential control, where applied voltage ϕ rather than σ is fixed. For illustration, we discuss the physical nature of the "ultimate anomaly," negative integral capacitance predicted by some recent analyses. We also show that σ-control anomalies can explain some experimentally observed features of $C(\phi)$.

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I. INTRODUCTION

Electrical double layers (DLs), the spatial charge separation arising at electrified interfaces, play important roles in surface electrochemistry, colloid science, plasma physics, and biophysics. A major thermodynamic characteristic of a DL is its specific differential capacitance, $C=\frac{1}{A}(\partial q/\partial\phi)$ (A is the surface area), describing the relationship between the surface charge, q, and the potential drop, ϕ. Starting with the classical work of Gouy [1] and Chapman [2] and Debye and Hückel [3] (GCDH), C became an important descriptor characterizing the structure of charged interfaces. In addition, as a typical linear-response function, it is closely related to interfacial stability and charging-induced surface phase transitions. These aspects of C, closely linked to the question of its admissible sign, are the major foci of this study.

The differential capacitance can be viewed from two physical perspectives: "potential control" (ϕ-control), where the applied potential difference is varied and the response is the charge acquired by the electrode [4–7], and "charge control" (q-control), where the interfacial electrode charge is controlled while ϕ adjusts in response. However, theoretical studies usually analyze DL behavior by imposing uniform (planar, spherical, etc.) surface charge-density distributions, σ. We term this "σ-control." Unlike ϕ- or q-control, σ-control is a purely theoretical construct, one not amenable to laboratory manipulation (see [8–11] for review). Numerous studies have shown that, for σ-control, there are surface charge-density domains for which the capacitance of a DL, or of its "diffuse" or "Helmholtz" (compact layer) components, is negative [12–15,5,6,16–22,7,23–26] (see the Appendix for a concise discussion of underlying phenomena).

There remains controversy regarding the interpretation of these results. Rigorous thermodynamic and statistical mechanical treatments, and analysis of electromechanical models, show that negative C is forbidden under "ϕ-control" [4–6,27,28]. If found under σ-control, negative C indicates instability and the possibility of phase transformation in a cell connected to a potential source [5–7]. If instability leads to a new equilibrium state rather than "short-circuiting" the DL, C is positive in both initial and final phases; transition occurs at fixed voltage with a discontinuity in q (analyses of electromechanical "toy models" [5,6,16,17,9] are illustrative). Treatments of another experimentally accessible situation, q-control, indicate that uniform distributions σ leading to $C(\sigma)<0$ are unstable [8,10,11]. Transition occurs under fixed electrode charge, while the potential drop ϕ behaves discontinuously. The final phase can be either homogeneous or nonuniform, depending on q. In what follows, we apply these ideas to the analysis of some recent results, both theoretical and experimental.

We first consider a recent study by Luo and Yu (LY) [29] suggesting that the stability conditions and the admissible sign of C could be different for two closely related cases: a single electrode (charged plane) in contact with the electrolytic half-space forming an "individual double layer" (IDL), and the electric cell with two electrodes (two oppositely charged planes) forming two double layers (TDL). In what follows, we demonstrate that qualitative differences between the IDL and TDL scenarios are illusory.

We then consider mechanisms responsible for σ-control anomalies and show that despite its artificiality, σ-control is a useful tool for understanding the nature of phase transformations under physically realizable conditions. We apply these observations to analyzing the "extreme" capacity anomaly predicted for some ionic DLs, negativity of the integral capacitance C_I.

Finally we consider how σ-control anomalies are reflected in capacitance behavior under ϕ-control.

II. CAPACITANCE OF A SINGLE INTERFACE AND OF AN ELECTRIC CELL

The suggestion (LY) that the restrictions on C can differ for the IDL and TDL scenarios relied on three arguments: (a) a Landau-Lifshitz (LL) thermodynamic analysis [4]; (b) an

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extension of local statistical analysis [16]; (c) an exactly soluble primitive electrolyte model [30,31,27,28,32,7]. We address all three arguments and describe their inconsistencies.

A. Landau-Lifshitz analysis: $C>0$ under ϕ-control

The Landau-Lifshitz (LL) derivation of the stability condition [4] for charged interfaces explicitly referred to two conductors in contact, i.e., to the IDL. LY suggested that LL's derivation of $C>0$ may not apply to TDL. In fact, LL analysis is readily extended to describe an electrode pair separated by electrolyte, i.e., the TDL. To avoid ambiguity, we almost literally follow the LL treatment.

The grand canonical potential for this system is (Eq. 25.6 of LL)

$$\tilde{\mathcal{F}}_s(q,\phi) = \mathcal{F}_s(q) - q\phi \tag{1}$$

with $\mathcal{F}_s(q)$ now the free energy of an isolated cell (TDL system) of fixed electrode charge, q. The $-q\phi$ term couples the electrodes to the potential source. The index s, dropped in what follows, indicates that all changes in the electrolyte due to external charges are localized in narrow "surface" (s) regions near the electrodes, i.e. the DLs. Equilibrium is defined by

$$\partial_q \tilde{\mathcal{F}}(q,\phi)|_\phi = 0, \qquad \partial_q^2 \tilde{\mathcal{F}}(q,\phi)|_\phi > 0 \tag{2}$$

The subscript ϕ explicitly accounts for ϕ-control implied by LL, who stated (just preceding Eq. 25.5) that the conductors' potentials were fixed. Here ϕ is the potential drop between two electrodes while LL identified ϕ with the potential difference between two conductors in contact (we later show that the latter is typically a particular case of the former). The first equation is simply

$$\phi_c(q) = \phi, \tag{3}$$

where

$$\phi_c(q) = \partial_q \mathcal{F}(q)$$

is the equilibrium potential drop across the cell when the electrode charge is fixed at q.

Equation (3) implicitly determines q as a function of the interelectrode potential drop; it states that the equilibrium q is attained when the equilibrium potential drop across the cell equals the applied voltage. The stability condition of Eq. (2) then yields

$$\partial_q^2 F(q)|_\phi = \partial_q \phi_c(q) = \mathfrak{C}^{-1} > 0, \tag{4}$$

where $\mathfrak{C}$ [33] is the total (nonspecific) differential capacitance of the whole cell with two electrodes (termed TDL in LY). Thus, the condition $C>0$ explicitly derived in LL for the IDL under ϕ-control also holds for TDL, an electrolyte sandwiched between two electrodes. In addition, only with two electrodes is it practical to study the electric properties of IDL. If the interelectrode distance d is large compared to the Debye length L_D, then $\mathfrak{C}$ is just the capacitance of two IDLs in series,

$$\mathfrak{C}^{-1} = \mathfrak{C}_1^{-1} + \mathfrak{C}_2^{-1}. \tag{5}$$

Assume $\mathfrak{C}_1$ of Eq. (5) is the contribution of the "working" electrode under investigation while $\mathfrak{C}_2$ describes the "reference electrode." By making $\mathfrak{C}_2 \gg \mathfrak{C}_1$, the TDL is effectively reduced to the IDL. The total applied voltage drop is then limited to the IDL belonging to the working electrode, essentially equivalent to the ϕ-control considered in the original LL analysis. The condition $\mathfrak{C}_2 \gg \mathfrak{C}_1$ can always be achieved by increasing the surface area of the reference electrode [34]. As the IDL is a limiting case of the TDL scenario, both IDL and TDL obey the same stability conditions under ϕ-control, reinforcing our point. The derivation of Eq. (4) makes it clear that if $\mathfrak{C} \leq 0$, the cell would be unstable relative to charging from the source: the release of the energy $-|\phi\delta q|$ due to electron transfer would overwhelm the increase of the internal free energy, $\delta F(q)$, due to charging of the double layers.

B. Diffuse layer under σ-control: Local and nonlocal statistical models

Consider the LY assertion that universal constraints on the admissible sign of the diffuse layer capacitance C_d [35] for IDL are derivable "using only arguments from electrostatics." Their analysis is based on the one-dimensional Poisson equation [29]

$$d_z^2 \varphi = -\frac{1}{\varepsilon\varepsilon_0}\rho(z) \tag{6}$$

subject to the boundary conditions

$$\varepsilon\varepsilon_0 \varphi'(0) = \sigma, \qquad \varphi(\infty) = \varphi'(\infty) = 0 \tag{7}$$

with σ a uniform planar charge density located at $z=0$, $\varphi(z)$ the total electrostatic potential, and $\rho(z)$ the charge density. Description of a DL entails unifying Eq. (6) with the statistical mechanics of electrolytes, a detail not dealt with consistently in LY [36]. In what follows, we show that implicit to LY's analysis is the assumption of a local relation between $\rho(z)$ and $\varphi(z)$ [i.e., $\rho(z)=\rho(\varphi(z))$] and that it is thus restricted to local statistical (GCDH-type) models.

To fully describe a DL requires augmenting Eq. (6) by an ionic equilibrium condition relating ρ and φ; in density-functional theory (DFT) (see [37] for review and references) terms this is

$$\frac{\delta \mathcal{F}[\{n_\alpha(\mathbf{r})\}]}{\delta n_\alpha(\mathbf{r})} + q_\alpha u(\mathbf{r}) - \mu_\alpha = 0, \tag{8}$$

where $\{n_\alpha(\mathbf{r})\}$ is the set of density distributions for cations and anions ($\alpha=\pm$) with electrochemical potentials $\mu_\pm$ [Eq. (8) is expressed in terms of the radius vector $\mathbf{r}$ instead of z to indicate the analysis is general, not limited to 1D systems], $u(\mathbf{r})$ is the potential of the external field, and $\mathcal{F}[\{n_\alpha(\mathbf{r})\}]$ represents the free-energy functional. The combination of Eqs. (6) and (8) already transcends pure electrostatics.

The treatment becomes especially simple in the "local-density theory" (LDT) [37] pioneered by GCDH. In this approach, the ionic density $\rho(\mathbf{r})=\Sigma_\alpha q_\alpha n_\alpha(\mathbf{r})$ can be found from Eq. (8) as the function of a single variable $\varphi(\mathbf{r})=u(\mathbf{r})+\nu(\mathbf{r})$ [$\nu(\mathbf{r})$ is the ionic contribution],

$$\rho(\mathbf{r}) = \rho(\varphi(\mathbf{r})). \tag{9}$$

Consequently, Eq. (6) reduces in LDT to an autonomous differential equation whose right-hand side depends on z only implicitly, through the unknown function $\varphi(z)$,

$$d_z^2\varphi = -\frac{1}{\varepsilon\varepsilon_0}\rho(\varphi(z)). \tag{10}$$

This leads directly to the condition $C_d^{\mathrm{LDT}} > 0$, positivity of the diffuse layer capacitance in the 1D LDT treatment [16].

Familiar transformations [38,39] yield

$$\sigma^2 = -2\varepsilon\varepsilon_0 \int_0^{\phi} \rho(\varphi) d\varphi, \tag{11}$$

where $\phi = \varphi(0) - \varphi(\infty)$ is the potential drop across the IDL. This determines the specific (per unit area) differential capacitance,

$$C_d(\sigma) = d_\phi \sigma = -\varepsilon\varepsilon_0 \rho(\phi)/\sigma, \tag{12}$$

where $C_d(0)$ is defined via l'Hôpital's rule: $C_d(0) = \sqrt{\varepsilon\varepsilon_0 |d_\varphi \rho||_{\varphi=0}}$. Since $\rho(\phi) \equiv \rho(z=0)$ and σ are of opposite sign, C_d is positive definite for any finite σ [16],

$$C_d^{\mathrm{LDT}}(\sigma) > 0. \tag{13}$$

Derived for LDT [i.e., using the relation (9)], this condition is not applicable to more general statistical models.

In nonlocal (NL) theories, which account for ionic correlations, Eq. (8) is a complex integro-differential equation and closed expressions such as Eq. (9) do not exist. Hence, σ and C_d cannot be expressed in the closed forms, Eqs. (11) and (12), and the condition $C_d^{\mathrm{NL}} > 0$ does not follow. For specificity, consider a nonlocal density-functional treatment that approximately accounts for ionic size correlations [40]. The ionic densities are $n_\pm(z) = n_\pm^0 \exp[\mp\beta q\varphi(z) - \beta\mu_\pm(z)]$ with $\mu_\pm(z)$ an excess chemical potential quantifying the correlations. The charge density, $\rho(z) = \Sigma_\alpha q_\alpha n_\alpha(z)$, can be written in the form $\rho = \rho(\varphi(z), z)$. As $\varphi(z)$ is unknown, z cannot be eliminated by the functional inversion $z = \varphi^{-1}(\varphi(z))$, and consequently ρ cannot be expressed as a function of φ alone. This example clearly demonstrates the previous argument.

The LY treatment formally used Eq. (11) (see Eq. 7 of LY) but dropped the arguments of ρ. This suppressed the fact that ρ is not generally a function of the single variable φ; consequently it is meaningless to use φ as an integration variable. After taking the ϕ derivative of this misleading equation, they obtained an equation (Eq. 8 of LY) identical to Eq. (11), with $\rho(\phi)$ on the right-hand side. However, this would be justifiable only if Eq. (9) were satisfied, i.e., within an LDT framework. Consequently, LY's condition $d_\phi\sigma > 0$ allegedly based "solely on the electrostatic nature of DL" is not generally supportable; their presentation simply reproduces a familiar result [16] [Eq. (13)] limited to local statistical models [41]. In fact, nonlocal models accounting for ionic correlation quite often lead to $C_d(\sigma) < 0$ [12,13,15,21,23–26,26]. Furthermore, we will see that even for LDT, where the diffuse layer contribution C_d is strictly positive, the total DL capacitance C can become negative due to the "anomalous behavior" of the compact layer contribution C_H [see Eq. (A5) and the associated discussion].

C. σ-control and the sign of C in primitive models of DLs

Another "proof" that C_d of an IDL must be strictly positive at fixed σ relied on the analysis of the "primitive electrolyte" between two hard oppositely and uniformly charged walls [30] (see discussions in [31,27,28,32,7,8]). The corresponding Hamiltonian (per unit area, A) is

$$H^\sigma = H' + \sigma f(\{z_i\}) + \frac{1}{2\varepsilon\varepsilon_0}\sigma^2 L. \tag{14}$$

H' is the ion-ion contribution in the absence of the external field, the second term describes ionic interaction with the electrode field, and the last term is the field's self-energy (i.e., the unshielded, electrolyte-free, interplate interaction energy); L is the interplate distance and $f(\{z_i\}) = (4\pi/\varepsilon)\Sigma q_i z_i$.

From standard statistical methods, the interplate potential drop is

$$\phi(\sigma) = \frac{\sigma L}{\varepsilon\varepsilon_0} + \langle f \rangle, \tag{15}$$

where

$$\langle(\cdots)\rangle = \frac{\displaystyle\int e^{-\beta A H(\sigma,\{\mathbf{R}\})}(\cdots) d\Omega}{\displaystyle\int e^{-\beta A H(\sigma,\{\mathbf{R}\})} d\Omega}$$

is a canonical average with integration over the system's configurational space, Ω, and $\beta = 1/kT$. The inverse capacitance $C_d^{-1} = \partial_\sigma \phi$ is

$$C_d^{-1} = \frac{L}{\varepsilon\varepsilon_0} - \frac{A}{kT}(\langle f^2\rangle - \langle f\rangle^2) \leq \frac{L}{\varepsilon\varepsilon_0}, \tag{16}$$

which is simply interpreted: electrolyte, by shielding the electric field, increases total capacitance relative to the "geometric limit," $C_G = \varepsilon\varepsilon_0/L$. The last term in Eq. (14) was omitted in [30]; in addition, the sign of the second term in Eq. (16) was inverted, yielding the erroneous result

$$C_d^{-1} = \frac{A}{kT}(\langle f^2\rangle - \langle f\rangle^2) > 0 \text{ (false condition)}. \tag{17}$$

LY assigned physical meaning to a "reduced" (missing the last term) version of Eq. (14) used by [30], assuming it described an IDL. This is not correct, as without ions, where both f and H' equal zero, the reduced Hamiltonian vanishes rather than describing the electric field energy due to a bare charged wall. Relying on the incorrect literature result Eq. (17), LY concluded that $C_d \geq 0$ for the IDL near a uniformly charged wall, i.e., under σ-control. Ironically, correcting the sign error in Eq. (17) (where the $L/\varepsilon\varepsilon_0$ term is still missing) would lead to the conclusion that an IDL's capacitance is strictly nonpositive, which would also be wrong.

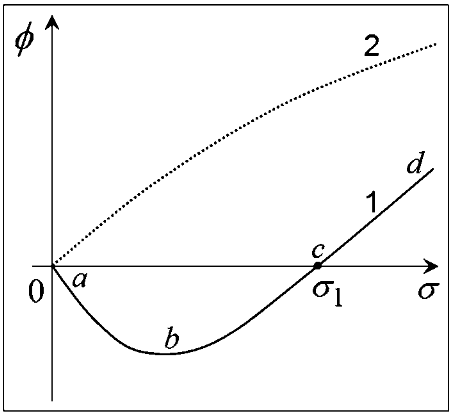

FIG. 1. Schematic fragments of the charging curves for the DL with negative integral capacitance $C_I=\sigma/\phi(\sigma)$ (curve 1) and the "normal" DL (curve 2). Along the segment *abc*, $C_I<0$, while the differential capacitance C is nonpositive along *ab*.

III. ORIGIN OF CAPACITANCE ANOMALIES UNDER σ-CONTROL AND THEIR MANIFESTATION UNDER ϕ-CONTROL

We have shown that both for a single interface (IDL) and for the electric cell (TDL), $C^{-1}\leq 0$ is permitted under the artificial conditions of σ-control (Secs. II B and II C), while C must be positive and finite under the physically achievable ϕ-control (Sec. II A). Thus, all the problems raised by the prediction of $C<0$ deal with the artificiality of σ-control; the distinction between IDL and TDL scenarios is not really relevant. Mechanisms leading to capacitance anomalies under σ-control are discussed in the Appendix; they can be interpreted either in terms of "relaxing gap capacitors" (RGC) or by focusing on the induced polarity of the electrolyte's charge distribution.

Despite being a fiction, σ-control remains a useful tool for analyzing the physics of charged interfaces. To demonstrate this, we first consider the possibly most intriguing result, some diffuse layer models' predictions of negative integral (total) capacitance (see, for example, [24,25]). We will address the question raised recently regarding the physical significance of such a prediction [24].

Secondly, we will discuss how the capacity anomalies under σ-control can be reflected in the observed $C(\phi)$ dependencies.

A. Negative integral capacitance and its physical significance

Negative integral capacitance is schematically illustrated by Fig. 1 (curve 1), characteristic of some symmetric electrolytes [24]. The region *ac* where ϕ is negative and $C_I=\sigma/\phi<0$ differs especially strikingly from "normal" behavior (curve 2). Before discussing the physical implications of this prediction, we verify its validity using an exactly soluble electromechanical "toy" model [42]. To reproduce charging behavior like that of Fig. 1, we use a slightly modified version of the toy model of [6], a "rigid" classical capacitor with an intercalated planar "elastic dimer." The two added "stops" limit the approach of the dimer planes to the capacitor plates (Fig. 2).

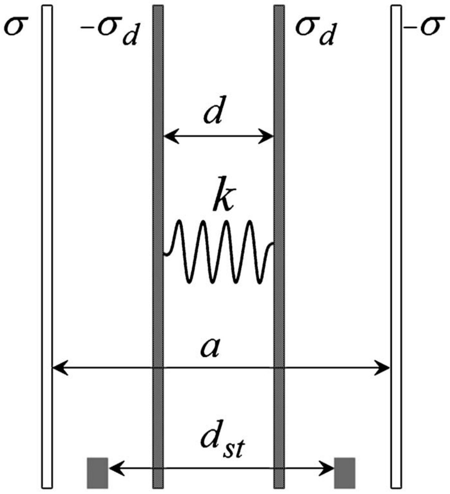

FIG. 2. Toy model of a textbook capacitor with an intercalated charged elastic planar dimer. k is the spring constant (per unit area) of the dimer, $|\sigma_d|$ and d are the fixed charge density on the dimer plates and the dimer's interplate separation, respectively, and $|\sigma|$ and a are the variable charge density and the fixed gap of the rigid capacitor.

This model clearly parallels the interpretation of the capacitance anomalies given in Appendix, part 2. The left plate represents the electrode, the right plate the linear component of the countercharge distribution (with a σ-independent centroid position), and the elastic dimer mimics the polarity of the induced charge distribution. The energy of this system (per unit area) is

$$W(\sigma,d)=\frac{\sigma^2}{2\varepsilon\varepsilon_0}(a-d)+\frac{(\sigma-\sigma_d)^2}{2\varepsilon\varepsilon_0}d+\frac{k}{2}(d-d_0)^2 \qquad (18)$$

(see Fig. 2 for parameter definitions). The condition $\partial_d W|_\sigma=0$ determines the equilibrium separation d

$$d(\sigma)=\begin{cases} d_0-\dfrac{\sigma_d^2}{2k\varepsilon\varepsilon_0}+\dfrac{\sigma_d}{k\varepsilon\varepsilon_0}\sigma, & \sigma\leq\sigma_{\rm st},\\ d_{\rm st}, & \sigma>\sigma_{\rm st}, \end{cases} \qquad (19)$$

where $\sigma_{\rm st}$, the solution to $d(\sigma)=d_{\rm st}$, is the least charge needed for the dimer plate to touch the stop. The corresponding potential drop is

$$\phi(\sigma)=\frac{1}{\varepsilon\varepsilon_0}\sigma a-\frac{1}{\varepsilon\varepsilon_0}P(\sigma), \qquad (20)$$

where $P(\sigma)=\sigma_d d(\sigma)$ is the dipole moment (per unit area) of the elastic dimer. The similarity to Eq. (A9) is obvious. To relate this model to a symmetric electrolyte (see, e.g., [24,25]), we consider a case in which $\phi(0)=P(0)=d(0)=0$, which requires that $\sigma_d^2=2ka\varepsilon\varepsilon_0$. The differential capacitance, here equal to the integral capacitance C_I, is

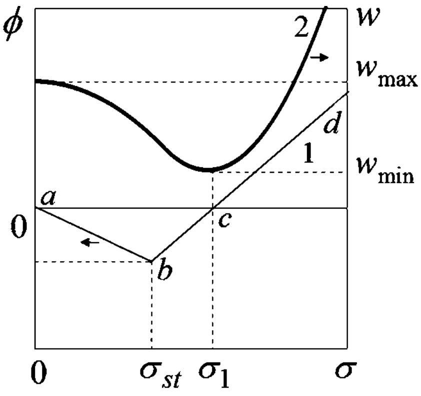

FIG. 3. Charging curve for the toy model of Fig. 2 (curve 1) and its electroelastic energy (curve 2), both in arbitrary units, with $a < 2d_0$. The slope discontinuity (point b) reflects the influence of the stop. After the dimer's plates reach the stops (i.e., for $\sigma \geq \sigma_{\text{st}}$), they are maximally separated and the capacitance becomes fixed and positive.

$$(C/\varepsilon\varepsilon_0)^{-1} = (C_l/\varepsilon\varepsilon_0)^{-1} = \begin{cases} a - 2d_0, & 0 \leq \sigma \leq \sigma_{\text{st}}, \\ a, & \sigma > \sigma_{\text{st}}. \end{cases} \qquad (21)$$

It is negative for $0 \leq \sigma \leq \sigma_{\text{st}}$ if $a < 2d_0$. The qualitative charging behavior for $a < 2d_0$ is represented by curve 1 in Fig. 3, a cusped version of curve 1 of Fig. 1.

Notice that $\partial_d^2 W(\sigma,d)|_\sigma = k > 0$, indicating that the equilibrium charge distribution [defined by the parameter d, Eq. (19)] is stable for all uniform σ, including the $C<0$ domain. This suggests that predictions of the same anomaly for the DL [24,25] are indeed consistent with ionic equilibrium in the σ-control framework. The corresponding energy profile

$$w(\sigma) = W(\sigma, d(\sigma)) \qquad (22)$$

is illustrated qualitatively in curve 2.

Now consider what happens under ϕ-control, where electrodes are connected to a source and their charge adjusts to minimize the total energy of the open system [compare with Eq. (1)],

$$\tilde{w}(\phi,\sigma) = w(\sigma) - \sigma\phi. \qquad (23)$$

When $\phi=0$, the energies of the open and isolated (σ-control) systems are both defined by $w(\sigma)$. However, for an isolated system with σ controllable, all points on the energy profile are accessible. In the open system, the equilibrium state, defined by the condition $\partial_\sigma \tilde{w}|_{\phi=0} = d_\sigma w(\sigma) = 0$, corresponds to the energy minimum $w_{\min}$; $\sigma=0$ describes a local maximum and is not accessible. Put differently, $C(0)<0$ describes an unstable "charge-thirsty" state, so that a short-circuited ($\phi=0$) cell charges spontaneously; the potential drop due to the electrode charge is exactly compensated by the dipolar contribution from the dimer,

$$\sigma a = -\sigma_p d_{\text{st}}. \qquad (24)$$

Increasing ϕ leads to further charging described by the "equilibrium" segment, cd, in both Figs. 1 and 3, where $C>0$. For the symmetric systems considered, the point $\sigma=0$, $\phi=0$ is the charging diagram's inversion point; when ϕ changes sign, σ changes discontinuously, with $|\Delta\sigma| \sim 2\sigma_1$. We expand on this in the next section in relation to $C(\phi)$ behavior.

For further discussion, it must be recognized that the separation of a DL into two components Eq. (A5) is a matter of convenience and only a negative total C (not its individual components) is truly anomalous [43]. Ionic models focus on the properties of the diffuse layer and thus on anomalies in C_d, and C_H is often viewed as a "buffer" ensuring that total capacitance $C>0$. However, the compact layer itself is also a RGC (see the Appendix) with the gap l_H depending on σ, and thus C_H cannot be assumed strictly positive [44]. Therefore, we consider the case when σ-control leads to a negative integral or more generally, differential, capacitance of the whole DL.

First consider the implications for the most common electrochemical setting, ϕ-control. Reference [24] noted that negative capacitance or negative differential capacitance does not imply energy storage but an energy source and is thus physically meaningless. Our analysis expands on this assessment. If a stable branch is present, the DL attains a local minimum with positive capacitance. A branch with $C<0$ would correspond to a "high-energy" state (a local maximum: curve 2 of Fig. 3), which would, were it achievable, be loosely characterized as an "energy source." However, the corresponding charge distributions are not attainable under ϕ-control. In other words, $C<0$ only has a virtual existence; its appearance under σ-control indicates the possibility of a DL phase transition. At equilibrium, apart from a narrow critical region surrounding $\bar{\phi}$ [7] (see Fig. 4), the DL behaves "normally," with $C>0$. The effect of criticality on the behavior of $C(\phi)$ is discussed below.

In addition to the electrochemical application just considered, $C<0$ could conceivably characterize an isolated colloidal particle. Such an interpretation is natural for finite radii spherical (see [24,45,26] and references therein) or cylindrical (see [46–49] and references therein) particles. In colloids, it is practically impossible to fix the potential drop between a particle and an electrolyte so ϕ-control is not readily achievable. For a particle of fixed charge, $C<0$ can indicate an unstable uniform distribution of σ under q-control [8]. Studying this requires augmenting the model to lift the restriction to uniform σ, and to permit "deformable" surface charge distributions and related conformational changes, reminiscent of electroelastic instabilities in membranes [10].

B. Peculiarities of $C(\phi)$ related to σ-control anomalies

Negative capacitance is associated with the decreasing portion of a nonmonotonic charging curve and is usually preceded by a local maximum. Figure 4 illustrates two charging curves $\phi(\sigma)$ displaying $C<0$ domains. The single extremum curve abc', clearly exemplified by the "elastic capacitor" (EC) model [5], has $C<0$ for $\sigma > \sigma_{01}$. Point c' corresponds to the "collapse" of the capacitor when $l=0$ and the plates of EC come in contact. The curve $abcd$ has two branches with $C>0$ separated by the region $\sigma_{01} < \sigma < \sigma_{02}$ with $C<0$. For a system connected to a potential source, approaching a local maximum in $\phi(\sigma)$ (or equivalently, a

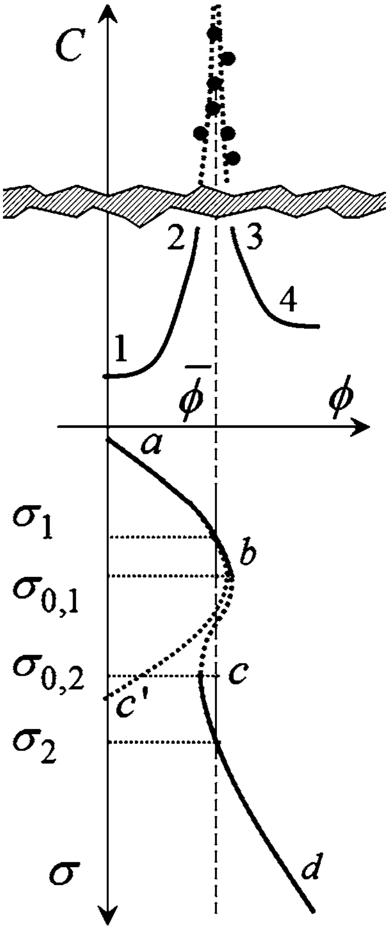

FIG. 4. Effect of bistability and phase transition on the behavior of $C(\phi)$ under ϕ-control. The curve abc' exhibits a single extremum typical of the EC model. The curve $abcd$, with its two extrema, displays bistability. The equilibrium states are $\sigma<\sigma_1$ and $\sigma>\sigma_2$. The corresponding segments of $C(\phi)$ are $1\leftrightarrow 2$ and $3\leftrightarrow 4$. Regions $\sigma_1\leq\sigma\leq\sigma_{0,1}$ and $\sigma_{0,2}\leq\sigma\leq\sigma_2$ are metastable; $\bar{\phi}$ is the critical voltage. Black dots represent fluctuations in the measured values of the apparent capacitance near the critical point, where σ behaves discontinuously and fluctuates strongly.

vertical asymptote in C) yields a charging instability. Once stability is lost, electrons from the potential source flow to the electrode, charging the DL. What happens next?

There are two main possibilities. In one, the increasing electric field will finally "short-circuit" the DL by triggering electron transfer across the interface (Faraday process). The equilibrium properties of DLs are typically investigated with the ideally polarizable electrode [38], where such behavior is avoided. The fingerprint of this case, where the breakdown of ideal polarizability is preceded by a charging instability, will be a sharp increase in C when σ approaches the boundary of the ideal polarizability range. This behavior, known for some interfaces of metal electrodes (i.e., Au, Pt) with solid electrolytes (AgCl, Ag_4RbI_5) [50,51], was rationalized in [14,5,10] using a microscopic approach accounting for electron relaxation effects.

A second, more interesting case, is that charging leads to a new equilibrium state without destroying ideal polarizability. A putative cause could be "steric" effects (see [11,52–54] and references therein) that restrict ionic densities near the electrode, leading to a new thermodynamically stable branch corresponding to $C>0$. This possibility can be investigated using the original model of the interface indicating the presence of $C<0$; however, the calculation needs to be extended to larger surface charge densities. If the second, increasing, branch $\phi(\sigma)$ is in a physically attainable σ-range, then the system is a probable candidate for phase transition.

How can bistability be reflected in capacitance behavior? For simplicity, assume experiments are conducted by measuring the variation in charge density, $\Delta\sigma$, due to a controlled finite variation, $\Delta\phi$, in the applied voltage, and determining capacitance as $C=\Delta\sigma/\Delta\phi$; $\bar{\phi}$ in Fig. 4 (the dashed vertical line) is determined by a Maxwell construction, analogous to standard van der Waals analysis of vapor-liquid transitions [37]. Capacitance increases (positive branch $1\rightarrow 2$ corresponding to the segment ab of the charging curve) as ϕ approaches $\bar{\phi}$. Near $\bar{\phi}$, a transition to the second stable branch occurs. Here, a small step $\Delta\phi$ leads to a large change in σ: $\Delta\sigma\sim\sigma_{02}-\sigma_{01}$. The corresponding points on an experimental C plot would be "outliers." Due to fluctuations, they would cluster in a narrow region and give rise to the tall narrow peak in Fig. 4. Further increasing ϕ produces the second stable ($C>0$) branch $3\rightarrow 4$. The details of the behavior along the wings $1\rightarrow 2$ and $3\rightarrow 4$ depend on specific equilibrium properties of the DL along the stable branches ab and cd, while a narrow peak in C is potentially a fingerprint of the phase transition.

The analogy with a van der Waals fluid is transparent. $C<0$ corresponds to negative compressibility and the charge discontinuity under fixed ϕ to the volume discontinuity under fixed pressure. Such a narrow peak with large capacitances (up to $2\ \mathrm{F/m^2}$) has been seen for interfaces between mercury and some ionic liquids [55]. While similar to the $C(\phi)$ plot of Fig. 4 and possibly indicative of a phase transition, less dramatic explanations have also been proposed [54]. The crux of this explanation is tied to the competition between ionic attraction to the electrode resulting in DL compression and a sharp increase in C at early stages of charging, and steric effects reversing this tendency at larger σ. Without arguing in favor of either of the two explanations, we would stress that the domain of $C<0$ and the existence of a stable branch are defined by exactly the same two competitive tendencies. In our view, it is very unlikely that all systems displaying such behaviors are invariably "tuned" to fit only one of the two pictures.

IV. CONCLUDING REMARKS

Thermodynamic stability conditions under ϕ-control are the same for a single electrode (IDL) and a cell (two electrodes, TDL): the total capacitance in both cases must be positive, clearly contradicting the conclusions of [29]. On the other hand, domains of negative capacitance are likely to occur in σ-based analysis of various electrified interfaces, both for IDL and TDL settings. The reason for these anomalies is the charge-induced compression of the effective gap of the DL, which can also be interpreted in terms of induced polarity of the screening charge distribution. These can be promoted by the electronic, ionic, and polarization responses to charging.

The notorious exceptions are local statistical models, where the condition $C_d^{\text{LTD}}(\sigma)>0$ is not a consequence of general thermodynamic restrictions, but is inherent in model limitations. Even here, the total capacitance under fixed σ can become negative, due to electronic and other relaxation effects leading to $C_H<0$. Predictions of $C<0$ domains under σ-control are indicative of charging instabilities and phase transitions under ϕ-control or lateral instability under q-control.

Although the appearance of capacitance anomalies can be considered ”normal” under σ-control [6,24], further work is needed to analyze the corresponding critical phenomena. To study the possibility of phase transitions with charge discontinuity, calculations must be extended to a wider range of charges, where steric-type contributions can lead to a second stable branch, $C>0$. Of special interest are cases in which this branch arises in charge ranges not “contaminated” by Faradaic processes. Here it is important to describe the compact layer contribution C_H in broader terms than the classical description as a constant-gap capacitor [44]. Accounting for microscopic effects can reduce C_H^{-1}, even making it negative, and thus shifting the critical range toward lower $|\sigma|$. Certain known patterns of $C(\phi)$, e.g., its steep increase in some solid electrolytes at the edge of the ideal polarizability range or the tall narrow peaks in some ionic liquids, can be explained in terms of charging instability under ϕ-control associated with the $C(\sigma)<0$ domains predicted to arise under σ-control. To discriminate between this and other interpretations will require a more consistent statistical mechanical analysis accounting for microscopic effects.

The implications of capacitance anomalies for the properties of colloidal macroparticles also deserve attention. Approximating the particle as a sphere or a cylinder (typical theoretical models of macroions) and assuming its total charge can be controlled (fixed), $C(\sigma)<0$ would indicate that the uniform distribution used in the theoretical analysis is unstable. Might this affect some observable properties of colloids? This can be addressed with more detailed models incorporating particle structure and interparticle interactions and which describe the charge distributions more realistically, lifting the uniform σ approximation.

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APPENDIX: TWO INTERPRETATIONS OF CAPACITANCE ANOMALIES UNDER σ-CONTROL

1. Relaxing gap capacitor (RGC)

The origin of $C<0$ under σ-control can be interpreted in terms of “electrostriction” of an interfacial capacitor, the charge-induced compression of its effective gap $l(\sigma)$ [5,6]. The charging relation for this RGC is simply

$$\varepsilon\varepsilon_0\phi(\sigma)=\sigma l(\sigma) \tag{A1}$$

and consequently

$$(C/\varepsilon\varepsilon_0)^{-1}=l(\sigma)+\sigma l'(\sigma). \tag{A2}$$

When the gap contracts upon charging, then $\sigma l'(\sigma)<0$. If

$$|\sigma l'(\sigma)|>l(\sigma) \tag{A3}$$

also holds, then the capacitance becomes negative. All existing predictions of $C<0$ can be rationalized in terms of the RGC (see [8,9,24] for review), recognizing that the effective gap of DL is defined by the centroids $z_{i,e}$ of ionic (i) and electronic (e) distributions $\rho_{i,e}(\sigma,z)$ induced by the electrode charge density σ,

$$z_{i,e}=-\frac{\int\rho_{i,e}(\sigma,z)zdz}{\sigma_{i,e}}, \tag{A4}$$

and associated with the positions of the electronic and ionic “plates” of the double layer. Here $\sigma_e=-\sigma_i=\sigma$.

Handling effects due to induced polarization is especially transparent in the conventional (although restricted) approach separating the DL into abutting layers, Helmholtz (H) and diffuse (d), i.e., two capacitors in series,

$$C^{-1}=C_H^{-1}+C_d^{-1}. \tag{A5}$$

Their dielectric constants are $\varepsilon_{H,d}$ and effective gaps are

$$l_H(\sigma)=z_H(\sigma)-z_e(\sigma), \tag{A6}$$

$$l_d(\sigma)=z_i(\sigma)-z_H(\sigma), \tag{A7}$$

where $z_H(\sigma)$ is the thickness of the Helmholtz layer (typically identified as the distance of closest approach of the ionic centers to the electrode’s atomic surface). The equilibrium behavior of the RGC and the existence of domains where $C<0$ have been illustrated in detail using the EC model and its various modifications [5,16,17,8]. However, EC-based models did not give rise to $C_I<0$. To present some background for a toy model demonstrating this anomaly, we now provide another interpretation, emphasizing the “polarity” of the induced charge-density distribution.

2. Induced polarity of the charge distribution

Consider the diffuse layer. For simplicity (but with no loss of generality), we identify $z=0$ with the Helmholtz plane, so that $l_d(\sigma)=z_i(\sigma)$. Now introduce

$$z_i^0=z_i(0)=\lim_{\delta\sigma\to 0}\frac{\int\rho_i(\delta\sigma,z)zdz}{\delta\sigma}=\int z[\partial_\sigma\rho_i(\sigma,z)|_{\sigma\to 0}]dz, \tag{A8}$$

the location of the ionic centroid in the limit $\sigma\to 0$. After adding and subtracting z_i^0, the charging relation Eq. (A1) can be written as

$$\varepsilon_d\varepsilon_0\phi_d(\sigma) = \sigma l_d(0) - P_i(\sigma), \tag{A9}$$

where $P_i(\sigma)=\int z[\rho_i(\sigma,z)-\rho_i^{(1)}(\sigma,z)]dz$ and $\rho_i^{(1)}(\sigma,z) = \sigma[\partial_\sigma\rho(\sigma,z)|_{\sigma\to 0}]$ is the linear approximation to the charge-density distribution. Global neutrality requires that $\int[\rho_i(\sigma,z)-\rho_i^{(1)}(\sigma,z)]dz=0$; $P_i(\sigma)$ is the specific dipolar moment of the ionic density distribution, accounting for its asymmetry with respect to the center of charge z_i^0. Then the capacitance is

$$[C_d(\sigma)/\varepsilon_d\varepsilon_0]^{-1} = l_d(0) - \partial_\sigma P_i(\sigma). \tag{A10}$$

While equivalent to the RGC interpretation, Eq. (A2), Eq. (A10) evokes quite a different image of a fixed-gap $[l_d(0)=\text{const}]$ capacitor with the polarizable insert. It is essentially equivalent to Eq. (16), with $l_d(0)$ playing the role of the interelectrode separation L, or to a classical "molecular capacitor" model (a grid of point dipoles between the plates of a parallel plate capacitor) [34,56]. The only difference among these three is in the nature of the induced polarization P. This interpretation emphasizes the induced polarity of the ionic charge distribution due to nonlinear charging effects, the nonmonotonic variation of the induced density profile. The condition for $C<0$ is now

$$\partial_\sigma P_i(\sigma) \geq l_d(0). \tag{A11}$$

It is important to recognize that even LDT models, such as Poisson-Boltzmann theory, can give rise to polarization increasing C above its "linear" limit. However, the condition Eq. (A11) is unattainable in LDT (see Sec. II B). Typical of nonlocal models, additional charge condensation (overscreening) near the electrode and the corresponding depletion in the "tail" region clearly increase the polarizability and make $C<0$ a possibility.

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[41] It is not uncommon that the predictions of local statistical models differ from those of nonlocal treatments and that they do not account for some important physical phenomena. Both Thomas-Fermi (TF) theory and its TF-Dirac-Weizsacker (TFDW) extension, local models of electron plasmas, have some highly unphysical implications such as vanishing (TF) or constant, metal-independent (TFDW) electron work functions and discontinuities in atomic electron density distributions (TFDW) [57]. Local ionic models of colloids do not account for attraction between identically charged particles [58–60] and charge inversion [61], effects observed experimentally and described theoretically by nonlocal analyses.

[42] "Toy models" demonstrating the possibility of DL anomalies without requiring the assumptions and approximations typical of statistical mechanical treatments have proven very fruitful. Early work [14,5] showed [using an "elastic capacitor" (EC) model] $C<0$ is possible under σ-control, proved this is not a model failing (see [6], p. 108), and that systems where $C<0$ under σ-control become "catastrophe machines" under ϕ-control [5,6]. Further modification of the EC model demonstrated the instability of uniform charge distributions in the isolated systems with $C<0$ and prompted the distinction between q- and σ-types of electric control [8].

[43] This is well understood, e.g., in the discussion of the equivalent electronic circuit with equation $I=C(d\phi/dt)$ (notations are ours) demonstrating the controversial nature of $C<0$ in [24], p. 9789; C clearly refers to the *total* differential capacitance of the *DL* (or the cell), not one of its components.

[44] Relaxation of z_e, the centroid of the electronic charge distribution (see Appendix 2), can lead to $C_H<0$ for some metals in contact with solid electrolytes (Au, Pt/AgCl, Pt/Ag_4RbI_5, etc.) in cathodic ($\sigma<0$) charge ranges [14,5,6,11]. Joint relaxation of z_e and z_H [Eqs. (A6) and (A7)] may result in nonmonotonic variation of C_H in contacts with surface-inactive electrolytes [62,6,17]; this typically increases at large negative σ and may become negative [6,17], a possibility overlooked previously [62] due to coarse-grained sampling of σ (for more examples, see [16,17,20,8]).

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