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"Squishy capacitor" model for electrical double layers and the stability of charged interfaces

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Negative capacitance (NC), predicted by various electrical double layer (EDL) theories, is critically reviewed. Physically possible for individual components of the EDL, the compact or diffuse layer, it is strictly prohibited for the whole EDL or for an electrochemical cell with two electrodes. However, NC is allowed for the *artificial conditions* of σ control, where an EDL is described by the equilibrium electric response of electrolyte to a field of fixed, and typically uniform, surface charge-density distributions, σ. The contradiction is only apparent; in fact local σ cannot be set independently, but is established by the equilibrium response to physically controllable variables, i.e., applied voltage ϕ (ϕ control) or total surface charge q (q control). NC predictions in studies based on σ control signify potential instabilities and phase transitions for physically realizable conditions. Building on our previous study of ϕ control [M. B. Partenskii and P. C. Jordan, Phys. Rev. E **77**, 061117 (2008)], here we analyze critical behavior under q control, clarifying the basic picture using an exactly solvable "squishy capacitor" toy model. We find that ϕ can change discontinuously in the presence of a lateral transition, specify stability conditions for an electrochemical cell, analyze the origin of the EDL's critical point in terms of compact and diffuse serial contributions, and discuss perspectives and challenges for theoretical studies not limited by σ control.

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I. INTRODUCTION

Electrical double layers (EDLs) play critical roles in electrochemistry, biology, colloid science, and plasma physics. Their major thermodynamic characteristic is the specific differential capacitance, $C=\frac{1}{A}\partial_\phi q$, which describes the relation between the total charge, q and the potential drop, ϕ (with A the surface area). As a typical linear-response function, it is intimately related to critical behavior in EDLs, the focus of our current investigation. This aspect of C is profitably illuminated by the interpretation of theoretical treatments manifesting domains of negative capacitance (NC). The differential capacitance can be viewed from two perspectives amenable to investigator manipulation: "potential control" (ϕ control) and "charge control" (q control) [1]. In the former, the applied potential is varied and the response is the charge acquired by the electrode; in the latter the interfacial electrode charge is controlled while ϕ adjusts in response. Under either scenario, thermodynamic stability requires that the EDL's capacitance be rigorously positive. However, many theoretical studies, and some simulations have analyzed electrical double layer behavior by imposing fixed and usually uniform (planar, spherical, etc.) surface charge-density distributions, σ, which we term "σ control." Unlike ϕ or q control, this is a purely hypothetical construct, one not realizable in the laboratory. Equilibrium analysis under these artificial conditions (where both the net charge and its local distribution are fixed), can validly predict negative capacitance, both for individual EDLs and for the electrochemical cell. Such a prediction does not disqualify the theoretical treatment, but rather is indicative of possible instabilities and phase transitions under the physically accessible q or ϕ control.

Recently we considered how σ-control peculiarities can inform our understanding of ϕ-controlled systems [1]. Under these constraints, we showed that σ-control manifestations of NC were the signature of a charging instability and/or a phase transition. Here we extend this investigation to analyze critical behavior under q control, addressing this and related questions from the perspective of exactly solvable toy models. To clarify the nature of σ control, as well as its physical distinction from ϕ and q control, in Sec. II we discuss the relationship of σ control to NC. In Sec. III we briefly review our recent study [1], describing the consequences of σ-controlled capacitance anomalies for ϕ-controlled systems. In Sec. IV we build on this study and illustrate the possible implications of σ-controlled NC for q-controlled systems. We extend the "elastic capacitor" (EC) toy model used to study ϕ-controlled systems and introduce a "squishy capacitor" (SC) representation, an extension of the EC that permits lateral instabilities. Section V focuses on NC-related instabilities, both for single interfaces and two-electrode cells. Section VI discusses the theoretical implications of NC and outlines open issues in simulations of NC-related critical behavior of electrified interfaces. Section VII provides a brief summary. The Appendix outlines physically important considerations for ensemble simulations under σ, q, and ϕ control.

II. σ-CONTROL AND NEGATIVE CAPACITANCE IN THEORETICAL STUDIES OF EDLs

The theory of ionic distributions near uniformly charged walls was initiated by Gouy [2] and Chapman [3] (GC); the corresponding approach based on local statistical models [1] is often termed Poisson-Boltzmann (PB) theory [4,5]. The inverse capacitance of the "diffuse" (d) ionic layer is defined as $C_d^{-1}=\partial_\sigma\phi_d$ where ϕ_d is the potential drop across the diffuse layer. In PB treatments, C_d is always positive. However,

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both extended PB analysis including ionic correlations [6–8] and Monte Carlo (MC) simulations of EDLs [9] led to the "unexpected and interesting result" [10] that under certain conditions ϕ_d decreases as the electrode σ increases. This result, equivalent to $C_d < 0$, has often been replicated (see [11–25], and references therein). While unusual, it was immediately seen to violate no physical principle [10] as long as the EDL's total capacitance is positive [26].

In the traditional (but restricted) treatment of the EDL, the diffuse layer is in series with a Helmholtz (H) (or compact) layer [27,28]

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

where C_H is often viewed as constant gap capacitor, with the gap, l_H, identified with z_H, the distance of closest approach of counterions to a metal electrode surface [29]. For ions of identical radius R_I this yields the classical Stern model [30] $C_H^{-1} = R_I / \varepsilon_H \varepsilon_0$ where ε_H is the compact layer's dielectric constant. Thus defined, C_H is strictly positive. As long as

$$C_H^{-1} > -C_d^{-1}, \tag{2}$$

the Helmholtz layer "buffers" the EDL keeping C positive despite the possible negativity of C_d. In terms of the Stern model this is equivalent to the following restriction on the diffuse layer contribution:

$$C_d^{-1} > -\frac{R_I}{\varepsilon_H \varepsilon_0}. \tag{3}$$

If Eqs. (2) or (3) were always obeyed, observing $C_d^{-1} < 0$ would pose no physical problems. However, systems of low ionic strength and high surface charge density, studied using the hypernetted-chain approximation, failed to satisfy Eq. (3) [10], casting doubt on the adequacy of the underlying theory. To resolve this issue, the possibility that NC was forbidden was investigated for "primitive ionic models" [10] and a hard-sphere mixture of ions and dipolar solvent molecules [31] between two oppositely charged walls with controllable charge density $|\sigma|$ (σ control, also termed fixed charge-density ensemble, FCDE, see Appendix, Sec. 1). Instead of the expected prohibition on NC, further studies [32,14,33] inspired by these papers led to a trivial capacitance restriction,

$$C(\sigma)^{-1} \leq \frac{L}{\varepsilon \varepsilon_0}, \tag{4}$$

with L the interplate separation and ε the background dielectric constant [34]. This condition simply indicates that electrolytic shielding of the electric field reduces C^{-1} relative to the geometric (no electrolyte) limit. It does not bound C_d^{-1} as suggested by Eqs. (2) and (3) and permits $C^{-1} \leq 0$ for both a two-electrode cell (represented by two charged walls) and for individual EDLs formed near each wall.

Both Monte Carlo simulations [13] and theoretical analysis [15] corroborated the possibility of $C < 0$ in FCDE treatments of EDLs. Microscopic studies of the metal electrons' contributions to the properties of EDLs [35–45] shed light on the role of the Helmholtz layer in the origin of NC. Electron density profiles near the electrode surface are strongly charging dependent, affecting both the "electronic plate" of the interfacial capacitor and the equilibrium positions of the electrolyte species in contact with the electrode (and thus z_H). These effects, completely suppressed for hard-wall electrode models [including the classical perfect conductor (PC) model], drastically alter compact layer properties, indicating that C_H can also be negative for contacts of metals with solid electrolytes [39,42,46] and solvents [40–42,44,45,47–50].

The relation of NC to charge-induced variation in the effective gap $l(\sigma)$ of the interfacial capacitor [39] is best understood in terms of a "relaxing gap capacitor" (RGC). Both components of C in Eq. (1) are essentially RGCs, with charging-dependent characteristic gaps [1]

$$l_H(\sigma) = z_H(\sigma) - z_e(\sigma), \tag{5}$$

$$l_d(\sigma) = z_i(\sigma) - z_H(\sigma), \tag{6}$$

and dielectric constants ε_H and ε_d (for simplicity, we ignore possible electron spillover into the diffuse layer). Here $z_e(\sigma)$ and $z_i(\sigma)$ are, respectively, the centroids of the electronic and ionic distributions

$$z_{i,e} = -\frac{\int \rho_{i,e}(\sigma,z) z dz}{\sigma_{i,e}}, \tag{7}$$

(where $\sigma_e = -\sigma_i = \sigma$); they are associated with the positions of the electronic and ionic "plates" of the EDL (see [1,51,52] for further details). NC can only arise if, for some σ domain (for specificity, the "anodic range," $\sigma > 0$), the effective gap $l(\sigma)$ contracts with charging (electrostriction) and the contraction rate is sufficiently high (see [1] and references therein),

$$|\partial_\sigma l(\sigma)| > l(\sigma)/\sigma. \tag{8}$$

Rigorous analysis has shown that local statistical (PB type) models, which predict l_d contraction for some σ domains, universally fail to satisfy Eq. (8) [1] and consequently never lead to $C_d < 0$ [53]. We now review the "elastic capacitor" (EC) toy model which unequivocally demonstrates that equilibrium gap relaxation can indeed lead to negative C under σ control, and use it to illustrate NC's implications for ϕ control. The EC also introduces our subsequent analysis, Sec. IV, of the squishy capacitor, designed to address the issue of NC for q control.

III. ELASTIC CAPACITOR TOY MODEL OF THE EDL: C ANOMALIES UNDER σ CONTROL AND THEIR MANIFESTATION UNDER ϕ CONTROL

A characteristic toy model representation of a RGC is an elastic capacitor [54,46,42], one plate of which is electrically grounded and the other plate attached to a spring (Fig. 1) [55]. We consider its equilibrium charging behavior under σ control, which naturally leads to NC. Then, using the EC toy model, we address another important puzzle, the apparent contradiction between the permissibility of NC under σ control, and its strict prohibition under ϕ control, derivable both thermodynamically [56] and from general statistical mechanical principles [57].

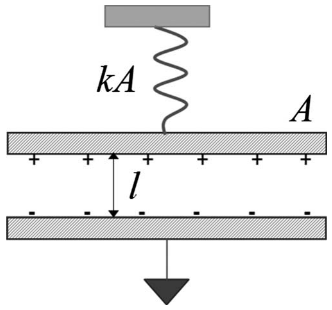

FIG. 1. Elastic capacitor: A is the area of its plate, k is the elastic bond constant per unit area, and l is the interplate separation.

A. EC and capacitance anomalies

Electrostriction potentially leads to negative C in a RGC if the rate of contraction with charging satisfies Eq. (8). The EC model provides a transparent example.

The specific (per unit area) electroelastic energy of the isolated EC with fixed charge density $\sigma = q/A$ (σ control) and spring constant k (also per unit area) is

$$W(\sigma,l) = \frac{\sigma^2 l}{2\varepsilon\varepsilon_0} + \frac{k}{2}(l-l_0)^2, \tag{9}$$

where l_0 is the gap for the neutral EC. Applying the equilibrium conditions $\partial_l W|_\sigma = 0$ and $\partial_l^2 W|_\sigma > 0$ the equilibrium gap is

$$l(\sigma) = l_0\left(1 - \frac{\sigma^2}{3\sigma_{cr}^2}\right), \tag{10}$$

where $\sigma_{cr} = \sqrt{2l_0 k\varepsilon\varepsilon_0/3}$. This solution is stable for all σ as

$$\partial_l^2 W(\sigma,l)|_\sigma = k > 0. \tag{11}$$

The equilibrium potential drop between the plates is

$$u(\sigma) = \frac{\sigma d(\sigma)}{\varepsilon\varepsilon_0} = \frac{\sigma l_0}{\varepsilon\varepsilon_0}\left(1 - \frac{\sigma^2}{3\sigma_{cr}^2}\right). \tag{12}$$

Consequently, the inverse capacitance is

$$C^{-1} = \partial_\sigma u(\sigma) = C_0^{-1}\left(1 - \frac{\sigma^2}{\sigma_{cr}^2}\right), \tag{13}$$

with $C_0 = \epsilon\epsilon_0/l_0$. C becomes negative for $|\sigma| > \sigma_{cr}$. The corresponding critical value of l is

$$l(\sigma_{cr}) = \frac{2}{3}l_0. \tag{14}$$

Early work [39,46], using these arguments, showed that NC is allowed under σ control, hence indicating that it is not a model failing (see [42], p. 108).

B. EC under ϕ control: sign of C and interfacial stability

The energy $\tilde{w}(\phi,\sigma)$ of an EC under ϕ control (the "grand canonical potential" [56]) is

$$\tilde{w}(\phi,\sigma) = w(\sigma) - \sigma\phi. \tag{15}$$

Here $w(\sigma) = W[\sigma, l(\sigma)]$ [see Eqs. (9) and (10)] is the energy of an isolated EC with charge density σ [58]; the term $-\sigma\phi$ couples the plates to a potential source [56]. Equilibrium conditions determine the electrode charge corresponding to the applied ϕ,

$$\partial_\sigma \tilde{w}(\phi,\sigma)|_\phi = \partial_\sigma w(\sigma) - \phi = 0, \tag{16}$$

$$\partial_\sigma^2 \tilde{w}(\phi,\sigma)|_\phi = \partial_\sigma^2 w(\sigma) > 0. \tag{17}$$

Equation (16) can be expressed as $u(\sigma) = \phi$: the equilibrium potential across an EDL, $u(\sigma) = \partial_\sigma w(\sigma)$ equals the applied voltage. The solutions of this equation, $\sigma = \sigma(\phi)$ describe the stationary charging points. When NC is present under σ control, multiple stationary solutions can exist. Equation (17) permits of solutions which are (at least locally) stable under ϕ control. It yields

$$\partial_\sigma^2 w(\sigma) = \partial_\sigma u(\sigma)|_{\sigma=\sigma(\phi)} = C_\phi^{-1} > 0. \tag{18}$$

The index ϕ denotes computation under ϕ control, where the applied voltage ϕ is controllably manipulated and the corresponding equilibrium charge measured. Negative values of C_ϕ, equivalent to $\partial_\sigma^2 w(\sigma) < 0$, would signify instability of the EC with respect to charge transfer between the potential source and the plates. Such σ are not attainable in equilibrium fixed voltage ensembles (FVE, Appendix, Sec. 3). The instability cannot occur in the FCDE, where charge is artificially constrained and neither plate is connected to a source. Thus, there is no contradiction between predicting $C(\sigma) < 0$ under σ control and the Landau-Lifshitz (LL) thermodynamic stability condition $C > 0$ [56], derived under ϕ control. Analysis of the EC [42,46,52,54] clearly demonstrates NC related instabilities under ϕ control [59]. This suggests alternative interpretations of interfacial phenomena, focusing on possible discontinuities and phase transitions [1]. We now consider a related question: how are σ-control anomalies manifested under the physically achievable setting of q control? The basic EC cannot treat this because its plates are laterally rigid. To circumvent this limitation, we introduce a new squishy capacitor model.

IV. SQUISHY CAPACITOR AND MANIFESTATION OF σ-CONTROL ANOMALIES UNDER q CONTROL

A. Stability conditions

The squishy capacitor is a system of N elastic capacitors connected in parallel (see Fig. 2). Their common fixed plate is electrically grounded, and the total charge on the electrically coupled movable plates (total area A) is fixed at q. The interplate distances l_i are always assumed small relative to plate dimensions so that edge effects can be neglected. The fixed plate represents the charged electrode while the relaxing plates mimic the electrolyte's counter charge distribution, thus accounting for two crucial features of an EDL's response to charging: relaxation of the equilibrium gap and the possibility of lateral gap variation. While the EC model illustrates charging instability (i.e., the discontinuity in q) un-

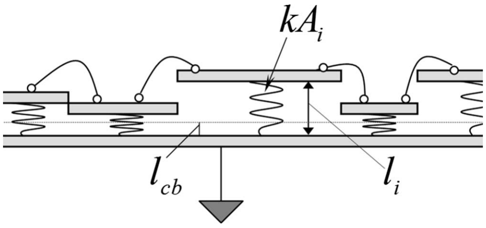

FIG. 2. Squishy capacitor: N elastic capacitors in parallel. A_i and l_i are the area and the interplate separation (gap) of the ith EC, k is the elastic constant per unit area. The dashed line indicates the position of a chock block, the lower boundary l_{cb} of the interplate separation. The line segments represent electric connections between the moveable plates.

der ϕ control (Sec. III B), the SC model releases the uniformity restriction, permitting lateral instability under q-control.

Assume all capacitors have the same gap l_0 when neutral and the same specific (per unit area) spring constant k; the specific energy of the isolated SC (q control) is then

$$W = \frac{\bar{\sigma}^2}{2G} + \frac{k}{2}\sum_{i=1}^{N} p_i(l_i - l_0)^2, \tag{19}$$

with $\bar{\sigma}=q/A$, the *average charge density* (equaling the actual density if all capacitor gaps, l_i, are the same), and $p_i=A_i/A$.

$$G = \sum_{i=1}^{N} G_i \tag{20}$$

is the total specific geometric capacitance of the SC, with

$$G_i = \varepsilon\varepsilon_0 p_i/l_i \tag{21}$$

the specific geometric capacitance of the ith EC. Dividing Eq. (19) by kl_0^2 and converting to dimensionless units yields

$$w = \frac{s^2}{2g} + \frac{1}{2}\sum_{i=1}^{N} p_i(1 - \xi_i)^2, \tag{22}$$

where $w=W/(kl_0^2)$ and $\xi_i=l_i/l_0$ are the reduced energy and gap, respectively.

$$s = \frac{q}{A}\sqrt{\frac{1}{\varepsilon\varepsilon_0 k d_0}} \tag{23}$$

is the reduced average charge density and

$$g(\Xi) = \sum_{i=1}^{N} \frac{p_i}{\xi_i} \tag{24}$$

is the SC's reduced specific geometric capacitance; Ξ is a configurational vector with components ξ_i. The stationary condition for the ith EC,

$$\partial_{\xi_i} w|_s = 0, \tag{25}$$

yields

$$\frac{s^2}{2\xi_i^2 g^2(\Xi)} + \xi_i - 1 = 0, \quad i = 1,2, \ldots N. \tag{26}$$

This, assuming ξ_i, $\xi_k \neq 1$ [60], yields the result

$$\left(\frac{\xi_k}{\xi_i}\right)^2 = \frac{1 - \xi_i}{1 - \xi_k} \tag{27}$$

one solution of which describes uniform compression

$$\xi_i = \xi_k = \xi. \tag{28}$$

Substituting Eq. (28) into Eqs. (26) and (24) and using the condition

$$\sum p_i = 1 \tag{29}$$

we find the s dependence of the interplate separation in the uniform state,

$$\xi(s) = 1 - s^2/2, \tag{30}$$

which is equivalent to the equilibrium solution for a single EC, Eq. (10) (in reduced units).

The dimensionless equilibrium potential $[v=u(kl_0^3/\varepsilon\varepsilon_0)^{-1/2}]$ for the uniform EC [see Eq. (12)] is

$$v(s) = s\xi(s) = s - s^3/2, \tag{31}$$

and the corresponding reduced capacitance is defined by

$$c^{-1}(s) = \partial_s v(s) = \left(1 - \frac{3}{2}s^2\right) \tag{32}$$

The critical reduced charge density s_{cr} is determined by

$$c^{-1}(s) = 0 \tag{33}$$

yielding $s_{cr}=\sqrt{2/3}$ and [compare with Eq. (14)]

$$\xi_{cr} = \xi(s_{cr}) = 2/3. \tag{34}$$

Under σ control the differential capacitance, c, becomes negative when $|s| > s_{cr}$. We now consider the stability of this uniform solution for different s in the physically admissible range

$$0 \leq |s| < \sqrt{2}. \tag{35}$$

At $|s|=\sqrt{2}$ the gap closes and the EC electrically shorts; larger $|s|$ under σ control is unattainable unless a chock is added (see below). Put differently, we assume the system is uniformly charged to a particular s with the mobile plates mechanically joined together, forming one rigid plate; then the plates are mechanically disconnected and allowed to equilibrate. As the solution, Eq. (30), is stable for the rigid plate EC for all s [see Eq. (11)], the only possible instability is related to the inhomogeneous relaxation of ξ_i and corresponding redistribution of charge. To analyze stability of the SC, consider the Hessian $N \times N$ matrix $H^{(N)}$,

$$H_{ij}^{(N)} = \partial^2_{\xi_i,\xi_j} w|_{\xi_i=\xi_j=\xi(\sigma)}, \tag{36}$$

where $i,j \in (1,N)$. Using Eq. (22) we find

$$H_{ij}^{(N)} = p_i\frac{2 - (3 - 2p_i)s^2}{2 - s^2}\delta_{ij} + (1 - \delta_{ij})\frac{2s^2 p_i p_j}{2 - s^2} \tag{37}$$

or

$$H^{(N)} = P \bullet T, \tag{38}$$

$$P_{ij} = \frac{p_i}{2-s^2}\delta_{ij}; \quad T_{ij} = [(2-3s^2)+2p_i s^2]\delta_{ij} + (1-\delta_{ij})2s^2 p_j. \tag{39}$$

We now show that the SC is unstable for

$$3s^2 \geq 2. \tag{40}$$

H is symmetric and thus its eigenvalues, λ_i, are real. Its determinant is

$$\det(H^{(N)}) = \prod_{i=1}^{N} \lambda_i = \det(P^{(N)})\det(T^{(N)}), \tag{41}$$

and

$$\det(P) = \frac{1}{2-s^2}\prod_{i=1}^{N} p_i > 0 \quad \text{for} \quad s^2 < 2, \tag{42}$$

the physically accessible range. The eigenvalues of T are

$$t_i = 2-3s^2, \;\; 1 \leq i < N; \;\; t_N = 2-s^2. \tag{43}$$

For $s \geq \sqrt{(2/3)}$ (Eq. (40)) $\det(T) < 0$ for even N. Then with Eqs. (41) and (42), we find $\det(H^{(N_{even})}) < 0$; consequently it has both positive and negative eigenvalues, a characteristic of instability (saddle point) [61]. The uniform solution becomes unstable at $s \geq s_{cr}$ with respect to nonuniform variation in ξ_i and a corresponding redistribution of charge [51,62,63]. From the above analysis, for odd $N = N_{even}+1$ the principal minor $[H]_{N,N} = \det(H^{N_{even}})$ is negative, also indicative of instability [61]. Thus, the condition Eq. (40) implies that the *SC* is unstable for all N. For illustration, we consider two representative cases, one where $N=2$ and the other where all N are identical.

B. Two coupled ECs

Consider two ECs ($N=2$) of different area, $p_1 = p$, $p_2 = 1-p$. Using Eq. (37) we find

$$H_{11} = p\frac{2-(3-2p)s^2}{2-s^2}, \quad H_{22} = (1-p)\frac{2-(1+2p)s^2}{2-s^2},$$

$$H_{12} = H_{21} = \frac{2s^2 p(1-p)}{2-s^2}, \tag{44}$$

$$\det|H||_{z=z(s)} = p(1-p)\frac{2-3s^2}{2-s^2}. \tag{45}$$

The determinant is negative for $s > s_{cr}$, indicating (for $N=2$) that in the critical range the uniform solution, Eq. (30), corresponds to a saddle point. Once again, onset of instability involves asymmetric variation in both ξ_1 and ξ_2, the details depending on p. For identical ECs ($p = 1/2$), loss of stability starts with antisymmetric variation in ξ_1 and ξ_2. Consider another limiting case, where one capacitor (e.g., EC$_1$) is much the smaller, $p \ll 1$. Here

$$H_{11} \approx p\frac{2-3s^2}{2-s^2}, \quad H_{22} \approx 1, \quad H_{12} = H_{21} \approx \frac{2s^2 p}{2-s^2} \tag{46}$$

and $H_{11} \leq 0$ for $s \geq s_{cr.}$. The small EC becomes unstable at the critical charge, while the large one remains stable, a result easily explained. The large capacitor's potential is practically unchanged if a tiny portion of its charge is transferred to its small companion. Hence, EC$_2$ plays a role of a potentiostat, effectively putting EC$_1$ under ϕ control. Thus, upon approaching the critical values of s and v, EC$_1$ becomes unstable with respect to gap contraction and corresponding charging of its plates from the "potentiostat" EC$_2$, essentially a special case of ϕ-control instability.

C. *N* identical coupled ECs

Here $p_i = p = 1/N$,

$$H_{ij} = t[(1+r)\delta_{ij} + (1-\delta_{ij})], \tag{47}$$

where

$$t = \frac{2s^2 p^2}{2-s^2}, \tag{48}$$

$$r = \frac{2-3s^2}{2s^2 p}. \tag{49}$$

One eigenvalue of Hessian (47) is $\lambda_1 = 1/N > 0$. The other $N-1$ are $\lambda_i = \frac{2-3s^2}{N(2-s^2)}$. Therefore, for $s \geq s_{cr}$ one eigenvalue is positive and the other $N-1$ are negative, indicative of instability. The eigenvector $\eta_1 = \{1,1,\ldots 1\}$ corresponding to λ_1 describes uniform compression. The other $\eta_i (i > 1)$ correspond to antisymmetric variation in ξ_1 and ξ_i. Now consider the stability of the uniform distribution relative to a harmonic perturbation

$$\xi_n = \xi_0 + \alpha\cos(qn), \quad q = 2\pi k/N,$$

$$n = 1,2,\ldots N; \;\text{with } k \text{ an integer}. \tag{50}$$

For small α the quadratic ($\sim\alpha^2$) contribution to the energy [Eq. (22)] is

$$w^{(2)} \sim \alpha^2 \frac{2-3s^2}{2-s^2}. \tag{51}$$

Thus, the energy change becomes negative at $s > s_{cr}$, which may indicate transition to a nonuniform phase, although other scenarios are possible (see discussion below).

V. MANIFESTATIONS AND CONSEQUENCES OF LATERAL INSTABILITY

A. Loss of stability under *q* control

So far we have considered linear instability. But what happens after stability is lost? As just seen, near the critical point s_{cr}, the interplate gaps of some ECs of the SC increase while others contract. No restoring force prevents contracting ECs from collapse and then short circuiting. A more interesting case relative to EDL phase transitions is a possible second stable branch with finite, positive capacitance. This is modeled by introducing a "chock block" (cb) bounding interplate separation from below by $\xi_{cb}=l_{cb}/l_0<\xi_{cr}$ (see Fig. 2), thus physically preventing collapse (at collapse $l_{cb}\to 0$). After stability is lost the contracting ECs abruptly transit to a "compressed" stable state with fixed interplate gaps, $\xi=\xi_{cb}$, a toy model analog of a surface phase transition [1]. In the EDLs the stable branch at larger σ can be produced, e.g., by "steric" effects, first recognized by [7] with respect to NC, preventing ions from accumulating near the electrode, thus slowing down or reversing the EDL's contraction rate [63–66], or by condensed molecular films forming on the electrode surface [67–70]. The equilibrium positions of the movable plates of the expanding ECs depend on s and ξ_{cb}. With further charging ($s>s_{cr}$) they gradually shift toward the chock. Typically, at some point s'_{cr} depending on p_i and ξ_{cb} they again become unstable and join the compressed state with $\xi=\xi_{cb}$, forming a "uniform compressed phase." The second critical point satisfies the condition $C(s'_{cr})^{-1}=0$. Although the mean charge density $s=q/A$ is fixed, stability loss is accompanied by discontinuous variation in the individual charge densities on the ECs as well as trans-SC potential $v(s)$. For specificity consider two identical ECs. The nonuniform state energy with the compressed gap fixed at ξ_{cb} and the relaxing gap ξ follows from Eq. (22). To within an insignificant constant, it is

$$w(\xi,\xi_{cb},s)=\frac{s^2\xi\xi_{cb}}{\xi+\xi_{cb}}+\frac{1}{2}(1-\xi)^2. \tag{52}$$

The local minimum can be found from

$$\partial_\xi w|_{s,\xi_{cb}}=0, \tag{53}$$

$$\partial_\xi^2 w|_{s,\xi_{cb}}>0, \tag{54}$$

where the critical (inflection) point s'_{cr} is defined by Eq. (53) and $\partial_\xi^2 w|_{s,\xi_{cb}}=0$.

This is illustrated in Figs. 3–6 where the transition steps are arbitrarily placed at the points s_{cr} and s'_{cr}, corresponding to loss of linear stability.

Due to fluctuations, the actual transitions occur at somewhat smaller s. Figure 5, which compares the energies of the nonuniform and uniform phases, clearly demonstrates the existence of a "metastable" region (curve 1, fragment bc) below s'_{cr}, where the local energy minimum describing the nonuniform state is separated by a barrier from the uniform state's lower minimum.

B. Does a total cell capacitance >0 ensure cell stability?

In practice, voltage is applied between two electrodes, and two double layers form, one per electrode. Consider electrolyte sandwiched between two electrodes, E_1 and E_2. If the interelectrode separation, d, is sufficiently large ($d\gg\lambda_D$ where λ_D is the electrolyte's Debye length), the whole cell's total inverse differential capacitance C^{-1} is

$$C^{-1}=C_1^{-1}+C_2^{-1}, \tag{55}$$

where C_i is the specific capacitance of the ith electrode ($i=1,2$). It is well known that ϕ-control stability requires $C>0$ (see [1] and Sec. III). However, does this ensure cell stability? Put differently, can a cell be stable if its total capacitance is positive while the contribution from one electrode is negative?

Without loss of generality consider a simple and instructive example (Fig. 7). EDL$_2$ is represented by a classical capacitor of constant gap a. Its positive capacitance $C_2>0$ is a buffer which guarantees that the total cell capacitance is positive. EDL$_1$, whose contribution can be negative under σ control, is modeled by the SC of the previous section. Would

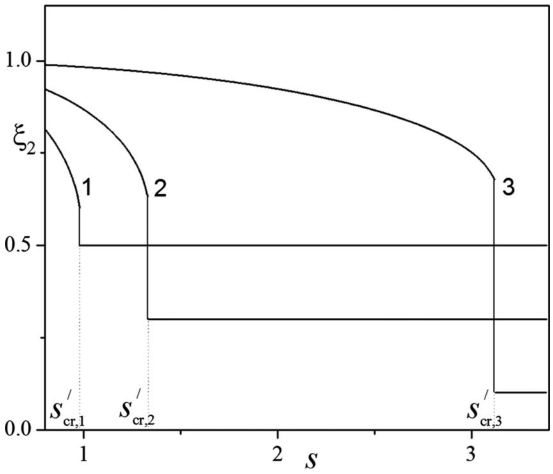

FIG. 3. Equilibrium position of the moveable plate for the squishy capacitor with $N=2$ and $p=0.5$, for three different positions of the chock: $\xi_{cb}=0.5$ (curve 1), 0.3 (curve 2), and 0.1 (curve 3). The average charge density s is taken in the "subcritical range," $s\gtrsim s_{cr}\sim 0.82$. The vertical steps represent a discontinuous displacement of the movable plate to the equilibrium position fixed by the chock. Horizontal fragments correspond to the "compressed" uniform phase, with both movable plates resting on the chock.

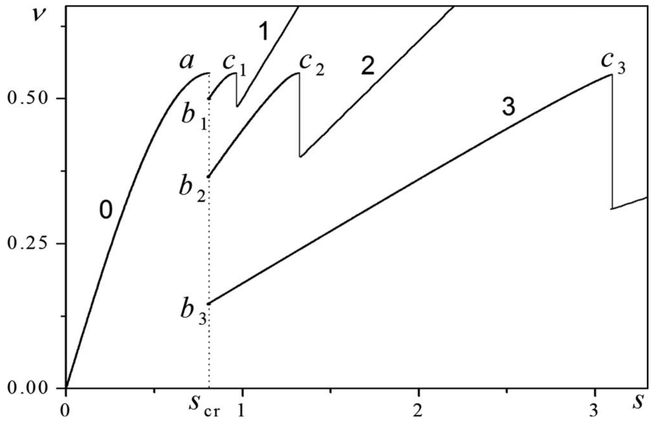

FIG. 4. Charging curves $v(s)$ for the SC with $N=2$ and $p=0.5$, for three positions of the chock: $\xi_{cb}=0.5$ (curve 1), 0.3 (curve 2), and 0.1 (curve 3). Curve 0 corresponds to the uniform state, rigid-plate elastic capacitor. The vertical line, $s=s_{cr}$, describes the transition from the uniform state (point a) to the nonuniform states (points b_i). Points c_i correspond to the critical charges $s'_{cr,i}$ shown in Fig. 3. The vertical steps describe discontinuities of v associated with the transition to the uniform condensed phase and the corresponding discontinuities of $\xi_2(s)$ (Fig. 3).

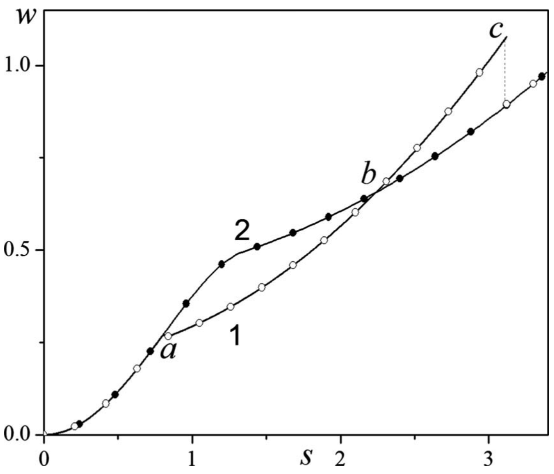

FIG. 5. Energies of the SC (curve 1) for $p=0.5$ and $\xi_{cb}=0.1$, and of the EC with the chock block (curve 2). The region ac of the curve 1 corresponds to the nonuniform phase. The vertical discontinuity at c describes the transition to the condensed uniform phase corresponding to the verticals steps in Figs. 3 and 4 (curve 3). The region bc is a metastable nonuniform phase whose local minimum is higher in energy than the global one corresponding to the condensed phase.

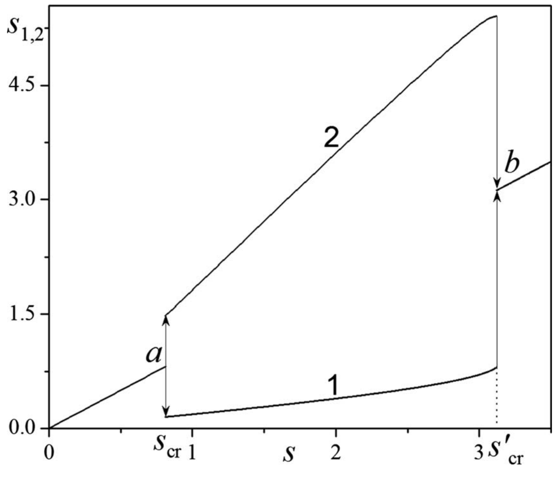

FIG. 6. Distribution of charge between two identical ECs comprising a SC. The parameters are the same as in Fig. 5. In the vicinity of s_{cr} (point a) the uniform state loses stability and the SC splits into two capacitors: one in the highly charged compressed state restricted by the block (curve 2): the other in the expanded state (curve 1). This nonuniform state loses stability near the point b corresponding to s'_{cr} and the condensed uniform phase is formed. Both transitions, a and b, are accompanied by discontinuities in the individual charge densities s_1 and s_2.

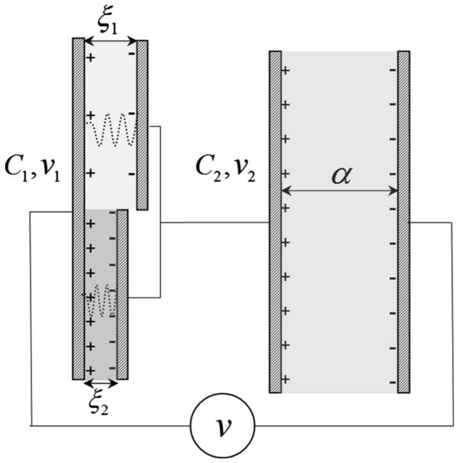

FIG. 7. Model of an electrochemical cell under ϕ control: The SC in series with the classical constant gap capacitor. The reduced potentials and interplate separations are defined in the text. The shading intensity reflects the electric field strength and the surface charge density. Despite nonuniformity in the charge and field distributions of the left-hand capacitor, the right-hand one is in a uniform state.

it be possible to observe $C_1<0$ if $C>0$? This question cannot be addressed by simply noting that EDL capacitances according to [56] must be positive. Indeed, the LL analysis [56] implied that the EDL obeys ϕ control, i.e., the whole voltage drop is confined to the EDL while the contribution of the second electrode can be neglected. In our case, however, only the total potential $v=u_1(\sigma)+u_2(\sigma)$ between two electrodes is fixed, while the individual components $u_1(\sigma)$ and $u_2(\sigma)$ are variable. The generalization [1] proves that C of the two-electrode cell is also positive, but it leaves open the behavior of the individual components, C_1 and C_2. Similarly, our demonstration that NC is forbidden for q control (Sec. V A) is inapplicable here as the potential is now controlled while electrode charge is variable. The total energy of the "open" cell (in contact with the potentiostat) is

$$\tilde{w}=w-sv+\frac{\alpha s^2}{2}$$

with w defined by Eq. (22); $\alpha=a/l_0$ (assuming uniform cell dielectric permittivity) and $v=\phi(kl_0^3/\varepsilon\varepsilon_0)^{-1/2}$ is the reduced external potential. From the equilibrium condition $\partial_s\tilde{w}|_v=0$ we find

$$s=\frac{v}{g^{-1}+\alpha},$$

where $g^{-1}\leq 1$ (the upper bound, 1, corresponds to the neutral SC). Thus, for $\alpha\gg 1$ we find $s\sim v/\alpha$, i.e., s is independent of the state of EDL$_1$. This effectively puts EDL$_1$ under q control, and the results of Sec. V A are applicable. In this limit the uniform state becomes unstable at $v\approx s_{cr}\alpha$ and negative C_1 is not observable. Formation of the nonuniform phase and its further transition to the condensed uniform state correspond directly with Figs. 3–6. The only difference is that the discontinuously varying potential (Fig. 4) is now u_1, with the free variable either the total (controllable) potential v or $s=v/\alpha$. Results with arbitrary α are similar. The critical charges s_{cr} and s'_{cr} (now produced by applying corresponding reduced critical voltages $v_{cr}=v(s_{cr})$ and $v'_{cr}=v(s'_{cr})$ are unaltered from those under q control. However, transition involves discontinuities in both v_1 and v_2, and s. Figure 8 illustrates this for the case $N=2$ and $p_1=p_2=0.5$, considered in Sec. V A.

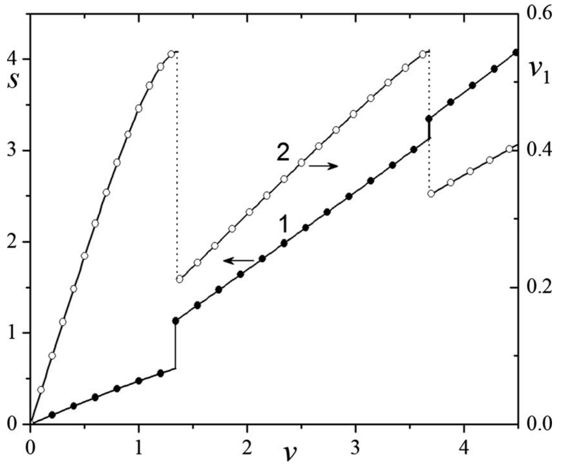

FIG. 8. Charge density s (curve 1, left-hand axis) and the potential across the SC, ν_1 (curve 2, right-hand axis), in the two-electrode cell, Fig. 7. The thickness parameter, $\alpha=1$.

Regardless of the details, we find that $C>0$ is no guarantee of cell stability: if one EDL exhibits NC under σ control, its uniform state loses stability near the corresponding critical point $v_{cr}=v(s_{cr})$ and undergoes a phase transition even if the system's total C under σ control is positive. Cell stability requires that

$$C_1^{-1}(s) > 0, \quad C_2^{-1}(s) > 0 \tag{56}$$

for all s corresponding to the voltage range considered. Despite superficial similarity, this differs from applying the stability condition (18) derived for a single interface to each EDL independently. As mentioned above, ϕ control of the EDL is implicit in the LL derivation; here neither individual contribution to ϕ is controlled. Assuming fixed total ϕ, each may change discontinuously due to instability. Furthermore, the LL derivation of the stability condition $C>0$ does not address predictions of σ-controlled NC. Our analysis indicates that $C_i>0$ in Eq. (56) corresponds to stable phases while $C_i(\sigma)<0$ (under σ control) is indicative of transition between stable states under physically realizable conditions.

C. Equivalent circuit for an EDL in the presence of lateral nonuniformity: The origin of the critical point

As just seen electrochemical cell stability requires that both EDL's contributions be positive. This speaks to the long-standing question of how predicted negativity of C_D or C_H, the individual components of the EDL described by Eq. (1), can possibly affect the properties of the EDL if the total C is positive [18,33,39,71]. Based on the similarity of Eqs. (1) and (55) and the arguments presented in Sec. V B, one might assume that a prediction of NC for one component, say $C_D<0$, leads to lateral instability of an EDL even if "buffered" by the second component, say $C_H>0$. However, there is an important difference. EDLs belonging to two different electrodes are uncoupled with respect to lateral fluctuations, so that EDL$_2$ [with $C_2(\sigma)>0$] is not directly affected by charge nonuniformity and electric field distributions in EDL$_1$ caused by its destabilization near the critical point [72]. In contrast, the diffuse and Helmholtz components of an EDL, Eq. (1), are not separated by bulk electrolyte; lateral fluctuations in one immediately affect the structure of the other. Consider a particular case, where $C_d^{-1}(\sigma)\leq 0$ exists under σ control while C and C_H are strictly positive. One can view this by sketching the Helmholtz layer as a uniform dielectric slab of thickness a. In a virtual standalone diffuse layer (e.g., primitive ionic model and in the limit $a\to 0$) the instability at $C_d^{-1}(\sigma)\to 0$ would lead to lateral nonuniformity of σ. However, with finite a the corresponding nonuniform electric field $\delta F(z,\rho)$ immediately penetrates the compact layer and increases its electrostatic energy by

$$\delta W_H \sim \int_0^a dz \int_A dA\, \delta F(z,x,y)^2 > 0. \tag{57}$$

This stabilizing contribution can shift or even prevent the transition. Similarly, nonuniformity in the compact layer triggered by its instability (if the $C_H\leq 0$ domain exists), would inevitably cause nonuniformity in the diffuse layer and a corresponding stabilization of its thermodynamic potential (assuming $C_D>0$) [73]. As a result, the two-capacitor model, Eq. (1), is particularly inappropriate for discussing possible instability due to lateral fluctuations (not to mention its general restricted applicability [74]).

For illustration, consider a toy model EDL, a *compact layer* with a fixed gap a, joined to a *diffuse layer* whose relaxing "squishy plate" mimics the ionic countercharge distribution, and whose neutral state gap is l_0. In the "normal" laterally uniform state this is seen either as a serial connection described by Eq. (1), or as a SC with the dimensionless gap $\alpha+\xi(s)$ ($\alpha=a/l_0$). For simplicity, both layers are assigned the same dielectric constant. Generalization to $\varepsilon_H\neq\varepsilon_d$ requires a trivial substitution $\alpha\to\alpha/\varepsilon_H$, $\xi\to\xi/\varepsilon_d$ and has no effect on the conclusions.

Here, unlike with a cell of two EDLs, negativity of one of the components (C_d in our example) is physically possible, and does not preclude EDL stability. Suppose instead that in this model the SC loses stability near the critical point $s_{cr}^{\mathrm{SC}}=\sqrt{2/3}$ of the *isolated* SC, where $C_d^{-1}\to 0$. The corresponding (virtual) lateral transition is not restricted to the SC alone, but also causes nonuniformities in the surface charge and electric field distributions in the adjoining compact layer [Fig. 9(a)], clearly demonstrating the origin of the stabilizing contribution δW_H, Eq. (57). Naturally, this stabilization, absent in the individual SC, must shift the critical point from s_{cr}^{SC}. Importantly, testing the possibility of a lateral transition immediately rejects the serial circuit representation, Eq. (1). The difference arises directly from the compact layer becoming itself laterally nonuniform, which would be impermissible in the serial model. Instead, the EDL is now described as a parallel connection of locally uniform fragments, individual ECs in series with the neighboring areas of the compact layer [Fig. 9(b)], i.e., a modified SC whose energy

$$w = \frac{s^2}{2g(\Xi+\alpha)} + \frac{1}{2}\sum_{i=1}^{N} p_i(1-\xi_i)^2 \tag{58}$$

is derived from Eq. (22) by substitution $\Xi\to\Xi+\alpha$ (equivalent to $\xi_i\to\xi_i+\alpha$) in g. Trivial analysis analogous to Eqs.

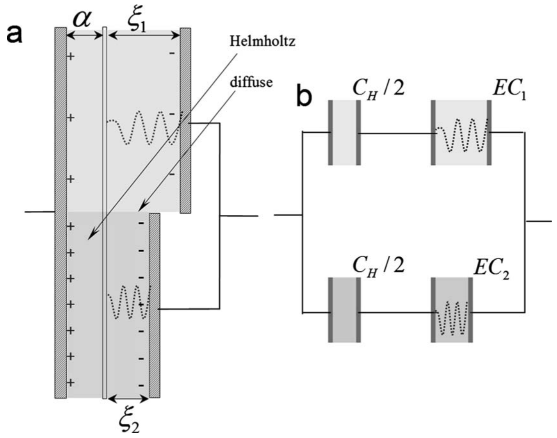

FIG. 9. Equivalent scheme of an EDL in presence of lateral fluctuations. (a) Model with two contiguous sublayers: classical compact layer capacitor with a fixed dimensionless gap, $\alpha=a/l_0$, and an SC representing the diffuse layer. The differences in gray shading indicate nonuniformity of the charge distribution and the electric field strength in both sublayers. Unlike in Fig. 7, nonuniformity due to lateral transition in the SC penetrates the compact layer.

(25)–(43) indicates the EDL's real critical point is

$$s_{cr}=\sqrt{\frac{2(1+\alpha)}{3}} \tag{59}$$

with $c^{-1}(s_{cr})=0$. This falsifies the hypothesis that $s=s_{cr}^{SC}$ is the EDL's critical point. As just indicated, the consequence is nontrivial. Using Eqs. (32) and (59) yields $c_d(s)\leq 0$ for $\sqrt{2/3}\leq s<\sqrt{2(1+\alpha)/3}$, a region where the EDL is linearly stable. From the perspective of the uniform phase preceding the transition [where Eq. (1) still holds], the critical point can be legitimately described as a tendency toward a mutual compensation between the two sublayer contributions:

$$C_d^{-1}\to -C_H^{-1}. \tag{60}$$

While negative C_d or C_H might appear nonphysical for q control, only the EDL's total capacitance has physical meaning and only it is required to be positive. Ignoring this can lead to serious confusion. For example, in a thermodynamic analysis [70] focused on possible orientational phase transitions in the compact layer, the sublayers were artificially separated implying that, for each of them, NC must be prohibited. This suggested that, at the critical point, both layers' contributions must be infinite,

$$C_H=\infty \quad \text{and} \quad C_d=\infty, \tag{61}$$

a very exotic condition, which would be extremely hard to achieve in practice. In addition, Eq. (61) is inconsistent with the exact example of EDL instability just discussed: according to Eq. (61), with C_H fixed the EDL should always be stable. The condition Eq. (60) (which only requires $C\to\infty$ and imposes no additional restrictions on the sign of components) is much "softer," since interfacial gap relaxation is a typical property of both sublayers [see the discussion of Eqs. (5)–(8)].

D. Relation between q- and ϕ-controlled instabilities of the SC

The EC demonstrates that NC in a σ-controlled equilibrium state implies physical instability upon switching to ϕ control. However, in an EC, charging associated with transition to a new equilibrium or a short-circuited state is inevitably uniform. How can the lateral flexibility present in the SC and in all realistic interfaces influence this transition? From Eq. (15), the reduced energy of the open system, a SC in contact with a potentiostat, is

$$\tilde{w}=w-s\upsilon \tag{62}$$

with w defined by Eq. (22). The charge density is no longer fixed, but determined from the equilibrium conditions

$$\partial_s\tilde{w}|_\upsilon=0 \tag{63}$$

and

$$\partial_s^2\tilde{w}|_\upsilon=c^{-1}>0 \tag{64}$$

leading to

$$s=\upsilon g(\Xi). \tag{65}$$

Solving the equilibrium equations

$$\partial_{\xi_i}\tilde{w}|_\upsilon=0 \tag{66}$$

jointly with Eq. (65) yields

$$2\xi_i^2(1-\xi_i)=\upsilon^2. \tag{67}$$

Remarkably, this equation describes the ith EC independently, indicating that under ϕ-control the individual components of the SC are effectively uncoupled. Each EC is individually charged by the potentiostat; the state of other ECs, unlike the case of q control, does not affect this process. After simultaneously losing stability at $\upsilon\sim\upsilon_{cb}$ all ECs contract until halted by the chock block. The capacitance in the new equilibrium state is

$$c^{-1}=\xi_{cb}>0. \tag{68}$$

Thus, under ϕ control, the squishy capacitor experiences a critical transition from one uniform phase to another, and the nonuniform two-phase state is not directly observable. We show later that this unusual property hints at ways to augment the model, which would make possible the study of two-phase states under ϕ control.

VI. DISCUSSION

A particularly thorny question in the theory of charged interfaces has been the meaning of NC and how this *physically* unrealizable prediction can inform *physical* understanding of interfacial phenomena (see [51,52,63] for reviews and references). Here, building on "toy model" insights, we discuss disputed issues and describe our approach to resolving them. Finally, we outline some perspectives on future theoretical study of NC-related critical properties.

A. Physical meaning and consequences of NC

Both general thermodynamic [56] and statistical [57] arguments show that the capacitance of an EDL (or of a two-electrode cell) is positive under ϕ control. In [10,31] where the NC issue was first clearly articulated, it was also suggested that NC was forbidden in theories of electrolytes in contact with uniformly charged walls, where σ rather than ϕ is fixed [Eq. (A1)]. This seductive conjecture, first believed exact and widely applied [18], was later found unsupportable [14,33,75]. Further work, based on MC simulation and exactly solvable toy models, indicated that NC is allowed for σ-controlled equilibria. How is NC, strictly forbidden under ϕ control (and, as just demonstrated, also under q control) permissible under σ control? Some studies [14,76] argued that the classical arguments were inadequate [56] and suggested NC should be permitted under ϕ-control (see [1,33,51] for critical discussion). The view we outlined previously [1,63] is simply summarized:

(1) While no strictures forbid NC under σ control, the latter hinges on two simultaneous constraints not generally physically realizable: (a) fixed q, and (b) fixed, usually laterally uniform, σ.

(2) In σ domains where $C<0$, relaxing σ control inevitably renders equilibrium states of NC unstable, with possible transition to a new, stable, state. Restriction (a) fails under ϕ control (fixed potential); q is unrestricted and adjusts to its optimal value [77]. In addition, the charging instability, leading to an abrupt change in q, generally violates restriction (b). In isolated systems with total charge fixed, the uniformity condition (b) fails due to spontaneous lateral redistribution of σ accompanied by abrupt variation in ϕ.

(3) In reality EDL capacitance, and that of the total cell sandwiched between two electrodes, must be positive. Equilibria can only be studied without restrictions imposed by σ control.

(4) Despite these basic limitations, predictions of NC under σ control are physically significant. They hint at instabilities and phase transitions under physically achievable conditions of ϕ control (a cell connected to a potential source) or q control (an isolated cell with total electrode charge fixed). Hence, they provide a foundation for more detailed studies of critical phenomena at charged interfaces.

This is clearly illustrated via toy models. Although not complete descriptions of instability and phase transitions related to the prediction of $C(\sigma)<0$, they provide a "sanity check," guidance to the forbidden and the observable, both theoretically and experimentally. They capture important features of real EDLs and analyze them rigorously. The elastic capacitor model accounts for an EDL's gap relaxation due to charging-induced variation in the electronic, ionic, and "polarization" charge distributions. Its study reveals the importance of clearly distinguishing between σ and ϕ types of electric control (see [46] where the terms were introduced). It rigorously describes the consequences of an EDL's "electrostriction," typical of electrified interfaces for some σ ranges, and unequivocally demonstrates that this can lead to $C<0$ for hypothetical equilibria *restricted by* σ control. Thus limited, predicting NC is commonplace and not indicative of any model failing [39,42,46]. These observations have been affirmed repeatedly, as typical of studies of ionic systems [13] and that NC prediction should be seen as a criterion validating a theoretical model, not a symptom of its failing [18]. However, that NC is allowable under σ control in no way implies it is *physically observable*. The EC model clearly showed that NC does not survive the transition to ϕ control. The corresponding *electroelastic* instability [59] is similar to one suggested as a mechanism for electroporation and rupture in lipid bilayers [54,78,79].

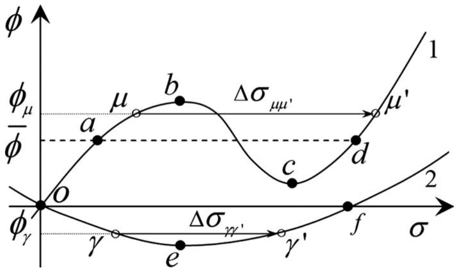

FIG. 10. Schematic representation of two typical charging curves displaying NC. Curve 1 contains a maximum, the NC range is segment bc and the second stable branch is cd. Curve 2 displays negative integral capacitance (see [1] for detailed discussion and the toy model displaying similar behavior). The NC segment is oe. The rest is explained in the text.

However, the EC model cannot describe instabilities of isolated interfaces with fixed total charge. In Sec. IV we introduced and studied the "squishy capacitor" model, allowing lateral charge redistribution and demonstrated that NC is also forbidden in an isolated, fixed q, system since transition to a nonuniform two-phase state near $\sigma=\sigma_{cr}$ is possible [Sec. V A]. Introducing a chock block mimics lattice saturation and other effects, potentially yielding $C(\sigma)>0$ and consequently a new stable branch at comparatively large σ, following the negative C domain. The simple example (two identical ECs in parallel) clearly exhibits lateral instability with abrupt ϕ transition to a nonuniform state, which evolves to a new uniform state at larger σ, and hints at the possibility of hysteresis.

This approach clarifies the issue of model (in)validation based on an NC prediction [10,13,14,18,31]. All treatments based (explicitly or implicitly) on σ control can result in NC; such predictions do not invalidate the underlying theoretical approach. How about ϕ control, where NC is strictly prohibited? Is a prediction of NC in the FVE model invalidating? Our answer is again "no." As demonstrated by the EC model (also see Appendix, Sec. 3), here NC may simply indicate that the selected stationary state is unstable (also the case under q control). Consider one example, a Monte Carlo simulation [13], which showed, using a specially designed primitive model, that NC is allowed under σ control [80]. Its charging diagram corresponds loosely to the segment $o\gamma e$ of curve 2 (Fig. 10). It was suggested [13] that this observation of σ-controlled NC supports the assertion that NC is permissible for ϕ control as well [14]. Clearly, this is not true. The state described by the point γ and belonging to the NC domain is only stable under σ control, and becomes unstable when the cell is connected to a battery at the same voltage ϕ_γ, and the artificial restrictions of σ control are released (see Appendix, Sec. 3). For the sake of generality we include a stable branch $e\gamma' f$ in the picture reflecting e.g., steric effects [63–66] (not included in [13]). Then, the EDL will transit to the stable point γ' at the same voltage, but with the charge incremented by $\Delta\sigma_{\gamma\gamma'}$. In fact, even at $\phi=0$ equilibrium corresponds to the polarized (charged) state f, not the neutral state O with $C<0$. The alternative to this transition (if there is no stable branch) would be electric breakdown of the EDL leading to a Faradaic process. Put differently, prediction of NC is never invalidating, but can prompt a search for different stable equilibria, corresponding to the same ϕ or q. Although apparently paradoxical, we tend to agree with [18] that the failure to observe NC is suggestive of model limitations, while its prediction suggests a more sophisticated and inclusive theory. For example, PB-type models neglecting ionic correlations never produce NC, while improved models, properly accounting for ion charge and size correlations, typically lead to $C_d<0$ in highly coupled EDLs. Similarly, on the metal side of the interface, C_H was always assumed positive until improved treatment of electronic contributions demonstrated limits to this assertion (see Sec. I and the following discussion).

B. Perspectives for future study of NC-related features

Historically, the theory of charged interfaces developed along two weakly integrated paths, focusing on two "sides" of the interface:

(a) *The* "electrolyte side," rooted in GC-type ionic models and molecular models of the Helmholtz layer. More comprehensive description of ionic charge and size correlations, more realistic description of the solvent, accounting for particle polarizability, improving interparticle interaction potentials, etc. all served to advance this line of research. However, the description of the electrode was generally oversimplified, usually by treating it as a hard charged wall with, at best, its conductive nature described by the PC model. Ionic models raised the issue of NC in EDL theory, and provided bulk data related to the appearance of $C_d<0$ for a range of systems and models. Some, such as [13,15] led to NC for the whole EDL. Recognition that early doubts regarding the soundness of NC predictions were unwarranted, inspired new theoretical efforts [18].

(b) *The* "electrode side," with more or less detailed and consistent accounting of electronic effects including, e.g., interaction of metal electrons with solvent molecules. Here, electrolyte treatment was usually oversimplified, often by focusing on metal/solvent interaction and describing the diffuse layer contribution by GC-type models. These studies highlighted the role of metal electrons in the effective gap relaxation in the compact layer, a feature ignored in group (a) theories. Incorporating charging-induced variation in the equilibrium solvent-electrode separation led to small and negative C_H^{-1} for metal/solvent interface in the anodic range, significantly improving agreement with experiment [50]. Similarly, treating electronic relaxation at metal/solid electrolyte interfaces, where solvent is absent, led naturally to diverging and negative C in the cathodic range, consistent with observation of sharply increasing ϕ dependence of $C(\phi)$ [50].

In summary, NC in EDL theory: is not generally forbidden in FCDE; is a typical feature of various RGC models; is commonplace for the individual components ($C_H<0, C_d<0$) and even for the full EDL in a range of models semi-independently describing two "sides" of the interface. Thus, we expect that more complete theories, consistently describing metal electrons and electrolyte, will quite routinely predict NC under σ control and related peculiarities under q and ϕ controls.

For at least two reasons simulations have rarely focused on NC-related critical properties: first because early studies viewed NC predictions as fundamentally erroneous; second, after the possibility of σ-controlled NC was recognized, due to the erroneous belief that it can be permissible under ϕ control [14]. Consequently simulation [13], and subsequent analytical study [15], demonstrating NC in the FCDE, ignored possible implications for ϕ-control criticality. These issues are still incompletely understood (see [1] for details). Thus, a recent call for "new computational efforts" motivated by a review of the NC controversy [18] seems appropriate and timely.

The study of NC related criticality requires well-constructed, simple models, which avoid complexities inherent to unified treatments. To treat microscopic relaxation of l_H [81], electronic contributions may be incorporated parametrically into $C_H(\sigma)$ (see [41,42,48,63,82,83]). An electrolyte model leading to $C_d(\sigma)<0$ can provide a further bias favoring NC. Following Torrie's insight [13], ionic models can be "tuned" to produce $C<0$ [80], thus circumventing complexity inherent, e.g., in incorporating ionic polarizability (known to promote NC [15]), and still be suitable for studying criticality.

With such a simplified model, critical behavior in isolated (q control) or open (ϕ control) systems can be efficiently analyzed. In these simulations the lateral charge distribution (in both cases), and the net electrode charge (ϕ control) must be treated on an equal basis with ionic distributions. A novel, relevant approach was recently developed for MC simulation of FVE with two electrodes [84]. Both ionic parameters and electrode charge density are free variables determined by equilibration. Here, combining the primitive electrolyte model with the hard charged wall model of the electrodes did not lead to NC under σ control; thus both canonical and grand canonical descriptions of the charging curve $\phi(\sigma)$ were equivalent. This approach is naturally applicable to studies of criticality for models displaying NC under σ control.

Consider Fig. 11, an "ionic analog" of Fig. 7. Here, analyzing lateral instability imposes technical requirements in MC simulations. The MC moves must sample the "macroscopically" inhomogeneous distributions of both σ and the ionic variables. To correctly compute energies, equipotentiality must be satisfied; the change in surface charge density, $\delta\sigma(x,y)$, must exactly (or very closely) shield the field due to perturbation of the ionic charge density, $\delta\rho(x,y,z)$. This requirement, possibly important even for the macroscopically uniform state simulated in [84] (where it was not imposed), appears critical for simulating lateral nonuniformity. Lateral periodicity of the simulation cell (see [84] and many other studies) introduces further complication predetermining the cell dimensions that properly accommodates the natural scale of lateral inhomogeneity is difficult. An alternate approach would be to use a finite spherical cell. Prelimi-

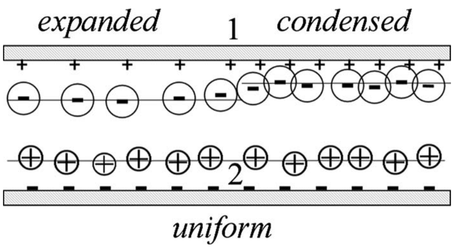

FIG. 11. Schematic representation of the two-electrode cell at the value of q such that $C_1(q/A)<0$ under σ control. The electrons and ions are distributed jointly to minimize the free energy and to keep the electrode surface equipotential. Two phases, condensed and expanded, correspond to two positions of SC's movable plates in Fig. 7.

nary σ-controlled simulations can guide studies of fixed charge ensemble (FCE, Appendix, Sec. 2) and FVE criticality. Consider a characteristic σ-control charging diagram with NC (Fig. 10, curve 1). The maximum is a typical consequence of interfacial gap relaxation, enhanced by ionic correlations and electronic contributions. The segment bc is the NC region; "steric" effects [63,64,66,85] can give rise to the stable branch at large σ. The point μ is a *locally* stable (metastable) state. However, transition to the globally stable state μ' with significant charge discontinuity $\Delta\sigma_{\mu\mu'}$ is expected under ϕ control. Similarly, a transition with abrupt potential change is expected under q control. Thus, the FCDE charging diagram can guide sampling of the configurational space in critical regions, where large fluctuations are important.

Some useful analogies can be also derived from the recent molecular-dynamics simulations of membrane electroporation [86], which demonstrated spontaneous stratification of the ionic distributions around the membrane coupled with the nonuniform membrane deformation, and consequent breakdown, when the critical voltage due to the ionic imbalance approaches the critical value V_{cr} [79].

Further insight may be garnered by modifying the SC model, so far used only for illustration. Our analysis of the ϕ-controlled transition, Sec. V D, shows that the inhomogeneous state does not arise for the model described in Sec. IV. The moveable plates are mechanically uncoupled, Eq. (22), leading to a set of N independent equilibrium conditions, Eq. (67). Coupling would impose an additional energy penalty for the phase "mismatch," effectively a "linear tension," the two-dimensional analog of the surface energy contribution in the theory of nucleation [87]. Incorporating this feature, important for analyzing surface phase transitions [67,69,88], would make the SC model more realistic. Using multiple ECs instead just the two of the examples could yield further insight. This introduces an "occupation parameter" $\zeta_c = N_c/N$, accounting for the population of ECs in the compressed ("c") state. Preliminary analysis shows that charging a SC of large enough N (with $p=1/N$) in the subcritical region $s \gtrsim s_{cr}$ leads to semicontinuous growth of ζ_c from 0 to 1, smoothing the abrupt transition in s'_{cr} of the $N=2$ case. This more closely corresponds to surface film condensation via nucleation and growth of a two-dimensional phase.

This analysis has mainly described metal/electrolyte interfaces. However, σ control is widely used, including multiple applications to the stability of membranes and colloids. Accounting for ionic correlations leads to some unusual properties, such as negative C_d, charge inversion and mutual attraction of similarly charged macroions (see [89,90] for review). As the underlying phenomena are similar to those leading to NC, scrutinizing σ control [91] could be illuminating.

VII. SUMMARY

Predictions of NC under σ control, with its fixed charge-density distribution, indicate instability and phase transitions for physically attainable constraints, with either the total charge, q, or the applied voltage, ϕ, controlled. NC must be a common feature in self-consistent treatments of metal electrons, ions, and solvent molecules. It can be interpreted as a consequence of charge-induced relaxation of the EDL's effective gap, and illustrated by electromechanical toy models emphasizing this feature. The elastic capacitor model showed that $C(\sigma)<0$ is admissible for σ-controlled equilibria, and must be commonplace for model studies of electrified interfaces. It also displays catastrophic behavior under ϕ control, hinting at instabilities and phase transitions in EDLs, similar to the electromechanical instabilities suggested as a mechanism for membrane electroporation.

The squishy capacitor model, Sec. IV, accounting for lateral charge redistribution in EDLs, demonstrates instability of the uniform state in isolated systems where total charge, q, rather than local charge density, σ, is fixed. It also shows that, for stability of an electrolyte sandwiched between two electrodes, the capacitance of each EDL must be positive. In other words, a positive total cell capacitance, while necessary, is not sufficient for stability. Transition in the ϕ-controlled cell is accompanied by abrupt change not only of q, but also of the individual potential contributions, ϕ_1 and ϕ_2, across the EDLs.

Despite apparent similarity, this analysis cannot be extended to the two-layer model of an EDL (compact and diffuse layer in series). Here, the layers are not spatially separated and they interact strongly. Essentially, they comprise a single EDL capacitor, for which only the total C must be positive; the critical point corresponds to $C\to\infty$. At the same time, the capacitance of individual components can become negative before stability is lost. The approach to the critical point can be legitimately described as mutual compensation between two contributions, $C_d^{-1}\to -C_H^{-1}$.

Simulating NC-related instabilities and phase transitions in isolated and open systems requires consistent sampling of the laterally nonuniform charge distributions on the electrode and in the electrolyte, securing equipotentiality of the electrode surface. The σ-controlled charging curve $\phi(\sigma)$ is an important guide in such studies. Existence of a $C>0$ branch at large σ, beyond the $C<0$ domain (typically associated with "lattice saturation" effects), indicates a second stable state crucial for the phase transition. An alternative would be electric shorting (breakdown) of the EDL associated with Faradaic processes. Extending the SC model can aid this research.

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APPENDIX: THREE TYPES OF ELECTRIC CONTROL AND NC-RELATED INSTABILITY

1. Fixed charge-density ensemble, σ control

"σ control" describes many theoretical studies of the EDL with the charge density $\sigma(r)$ treated as an independently controllable variable, usually implemented as a uniform (σ =const) distribution, planar, spherical or cylindrical. This simple description can be modified to account for interfacial polarizability, e.g., for metal/electrolyte contacts. Although theories of EDLs were largely triggered by the electrochemical applications, most ionic models did not really account for the electrode's metallic nature. Assume the PC model of classical electrostatics, with the metals as media of dielectric constant $\varepsilon_m = \infty$. For a finite ε solvent, there is a dielectric discontinuity; the image effects substantially complicate computations. To avoid these, many studies [92] treated an idealized approximation: dielectric equivalence of the charged wall and the solvent. Only then, with surface polarization artificially suppressed, does the actual charge density equal the preset value σ. Dielectric discontinuity requires local variation in σ induced by the counterions' electric field, conveniently described by images. Thus, for the PC model of metals the surface charge density is totally reflective of the nonuniform charge distribution due to counterion images. It shields the external fields keeping the surface equipotential [93], and fluctuates due to the thermal movement of the ions. From this perspective, σ control is equivalent to requiring that the temporal average of the local $\sigma(r,t)$ is fixed and uniform. In EDL simulations accounting for image effects, pioneered by Torrie *et al.* [94], this is usually achieved by fixing the specific (per unit area) excess of the ionic charge in the electrolyte. As outlined in Sec. VI later analysis demonstrated that the images need not forbid $C_d < 0$ at metal/electrolyte interfaces (see [11,24,25,95] and references therein), consistent with Eq. (4) [34]. Accounting for image effects or, even better, for the microscopic electronic properties of the electrode surface, is crucial to understanding σ control and its relation to the q and ϕ types of control (see Secs. II and VI B).

2. Fixed charge ensemble, q control

q-control describes isolated systems with fixed total electrode or particle charge. For a macroscopically stable homogeneous distribution σ and q controls are equivalent. The differences matter in describing instabilities and surface phase transitions, where a laterally nonuniform (e.g., two-phase mixture) state is preferred. Here only the q-control description of the isolated system is proper. To analyze instabilities at the metal/electrolyte interfaces consistent treatment of electron redistribution is critical, regardless of how surface polarization is treated. For a PC, spontaneous lateral redistribution of σ must be related to the redistribution of charges in the electrolyte, reflecting the law of images, keeping the electrode's surface equipotential. As described in Sec. VI B, this requirement, automatically accounted for in our "squishy capacitor" toy model, may create additional difficulties in modeling surface instabilities and phase transitions.

3. Fixed voltage ensemble, ϕ control

Consider electrolyte sandwiched between two electrodes connected to a potentiostat (battery). Electrical control of the cell is maintained via the electronic subsystem of the electrodes. The real controlled variable is the difference between the electrochemical potentials of the electrons in two cell electrodes, μ_1 and μ_2, associated with their Fermi levels [33,96]. Assuming identical electrodes (thus avoiding contact phenomena complications), the electrochemical potential difference equals the voltage

$$\phi = \frac{\mu_1 - \mu_2}{e},$$

where e is the protonic charge. Equilibrium conditions establish q and its surface distribution σ. Under ϕ control the potential difference is fixed and each electrode surface is equipotential [93]. The thermodynamic potential is now (see [56] and also [1,33] for details)

$$\tilde{\mathcal{F}}(q,\phi) = \mathcal{F}(q) - q\phi, \tag{A1}$$

where $\mathcal{F}(q)$ corresponds to the canonical ensemble, FCE. The contribution $-q\phi$ couples the potentiostats and the electrodes. Equilibrium is defined by [see also the discussion of Eqs. (15)–(18)]

$$\partial_q \tilde{\mathcal{F}}(q,\phi)\big|_{\phi} = 0, \quad \partial_q^2 \tilde{\mathcal{F}}(q,\phi)\big|_{\phi} > 0. \tag{A2}$$

The first equation is equivalent to

$$\partial_q \mathcal{F}(q) = \phi \tag{A3}$$

and defines the stationary charging states $q = q(\phi)$ corresponding to a fixed ϕ. The second yields

$$\partial_q^2 \mathcal{F}(q)\big|_{q=q(\phi)} = C^{-1} > 0. \tag{A4}$$

Evidently, $C^{-1}(q) < 0$ would indicate that a corresponding stationary point q is *maximal*, and not physically accessible under ϕ control. This observation explains, for example, why γ' (Fig. 10, Sec. VI B) is the only state stable at the voltage ϕ_γ, while another stationary point, γ, is only accessible under the artificial restrictions of σ control.

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[59] The physical reason for the instability of the EC under ϕ control is the steep $\sim\phi^2/l^2$ increase in the attractive electrostatic force at small separations l. Increasing ϕ initially leads to a continuous shift of the relaxing plate; it also flattens the local minimum corresponding to its equilibrium position. Near the critical voltage, $\phi_{cr}=u(\sigma_{cr})$, the local minimum disappears completely (the inflection point). This leads to collapse when the gap and the charge on the plates change discontinuously [1,51]). A small change in the controlled parameter ϕ leads to a dramatic discontinuous change in the equilibrium state of EC, similar to Zeeman's "catastrophe machine" and the Euler buckling instability [100]. Such behavior is interpretable in terms of simple models with variable charges bound to their equilibrium positions by linear restoring forces [52,101,102].

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[73] It is worth noting that the so-called "molecular models" simulated the compact layer as a two-dimensional lattice of "molecular dipoles" inserted between two conductors, the electrode and the solvent, often treated in the PC approximation (with $\epsilon=\infty$). In this approximation, a region of $C_H \leq 0$ under σ control would signify phase transition in the compact layer. However, in the PC model, which effectively places all the countercharge in the Helmholtz plane, C_d vanishes, and the compact layer is simply equivalent to the EDL.

[74] Here, we ignore more conventional reasons for the inconsistency of two-layer EDL models, among them, specific ionic absorption on the electrode, strongly dissimilar sizes of cations and anions (which can be partially overcome by corresponding modification of $z_H(\sigma)$ [85] or by considering a restricted σ range where one counterion species dominates [13]), penetration of the electron-density distribution beyond the limits of the compact layer, etc. [66,104].

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