

# Effect of finite ion sizes in an electrostatic potential distribution for a charged soft surface in contact with an electrolyte solution

Sourayon Chanda and Siddhartha Das\*

*Department of Mechanical Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G8*

(Received 29 October 2013; published 13 January 2014)

We provide a theory to analyze the impact of finite ion sizes (or steric effect) in electrostatic potential distribution for a charged soft surface in contact with an electrolyte solution. The theory is based on a free energy model that appropriately accounts for the contribution of finite ion sizes as well as the structural characteristics of a soft interface, represented by a combination of a rigid surface and a fixed charge layer (FCL), with the FCL being in contact with an electrolyte solution forming an electric double layer (EDL). This FCL contains a particular kind of ion which is impermeable to the electrolyte solution, and this impermeability is quantified in terms of the corresponding Donnan potential of the “membrane” represented by the FCL-electrolyte interface. We find that consideration of the finite ion size increases the magnitude of this Donnan potential, with the extent of increase being dictated by three length scales, namely, the thickness of the FCL, the thickness of the electrolyte EDL, and the thickness of an equivalent EDL within the FCL. Such regulation of the Donnan potential strongly affects the distribution of the permeable electrolyte ions within the FCL, which in turn will have significant implications in several processes involving “soft” biological membranes.

DOI: [10.1103/PhysRevE.89.012307](https://doi.org/10.1103/PhysRevE.89.012307)

PACS number(s): 82.45.Gj, 82.45.Mp

## I. INTRODUCTION

As an electrolyte solution comes in contact with a charged or ionizable solid, there is the formation of an electric double layer (or EDL), which refers to an immobile (Stern) layer and a diffuse layer of charges developed at the electrolyte-solid interface, screening the charge present at this interface [1,2]. This apparently simple picture, often mathematically described through the classical mean field Poisson-Boltzmann (PB) model [1,2], has attracted huge interests for more than a century owing to the massive number of applications that invariably involve the presence of such a solid-electrolyte interface [3,4]. In fact, such application requirements, particularly those involving nanoscale transport of electrolyte solutions [5–7], have led researchers to look beyond this simple description of the EDL. Such alterations can stem from accounting for usually neglected effects pertaining to components such as the solvent (e.g., solvent polarization [8,9] or the presence of multiple solvents [10,11]), electrolyte ions (the effect of finite ion size [9,11–14] or the effect of multivalent ions [15]), or the substrate (of varying polarizability [16,17] or varying chemical and physical structure [18–20]), etc.

Here we study a problem that combines two of these situations, namely, we investigate the effect of finite ion sizes (or steric effect) in dictating the electrostatic potential distribution of a soft interface in contact with an electrolyte solution. In the context of EDL theories, a soft interface is typically represented by a rigid surface covered by a layer of polyelectrolytes (this layer is grossly approximated as the surface charge layer), which can be ion penetrable, leading to an electrostatic potential distribution that is distinctly different from that in an EDL in contact with a bare rigid surface [21–24]. Such a representation of charged soft interfaces, in particular, the corresponding electrostatic behavior in the presence of an

electrolyte solution, has been motivated by several biological and chemical applications, such as the electrokinetics of biological cells [25], the effect of EDL in bacterial adhesion to surfaces [26,27], charging and swelling of cellulose films [28], etc.

A model of EDL electrostatics of soft interfaces has been primarily developed by Ohshima and co-workers [21,22,24,29–31]. Most of the analysis is based on the simplest situation, namely, the case where there are fully ionized groups of valence  $Z$  that are distributed at a uniform density  $N$  in the surface charge layer (accordingly, henceforth the surface charge layer is called the fixed charge layer or FCL), and the plate core (the hard part) is uncharged (see Fig. 1). Further simplification is ensued when it is assumed that the relative permittivity within the FCL is identical to that of the electrolyte solution [21,32]. The most important consideration in such a model is that these ions within the FCL are impermeable to the electrolyte that is in contact with the FCL, whereas the electrolyte ions can freely permeate between the FCL and the electrolyte. Therefore, the interface between the FCL and the electrolyte acts as a hypothetical selectively permeable membrane, and consequently the corresponding quantification is expressed in terms of the Donnan potential  $\psi_D$  [2,33]. Mathematically,  $\psi_D$  is the potential deep inside the FCL for the case where the FCL thickness ( $d$ ) is much larger than the electric double layer (EDL) thickness  $\lambda$  (quantifying the ion distribution within the electrolyte) [21]. These two length scales ( $d$  and  $\lambda$ ), along with a third length scale, namely, an equivalent EDL thickness  $\lambda_{\text{FCL}}$  within the FCL, dictates the electrostatic potential distribution (and hence  $\psi_D$ ) within the FCL as well as within the electrolyte in contact with the FCL. As for the classical problem of rigid surface electrokinetics, for soft interfaces as well the knowledge about the corresponding electrostatics has been extensively used to model issues such as electrostatic interactions between two similar or dissimilarly charged soft interfaces [34] electrophoretic mobility of soft particles [35], and other related electrokinetic phenomena [36], etc.

\*sdas1@ualberta.ca

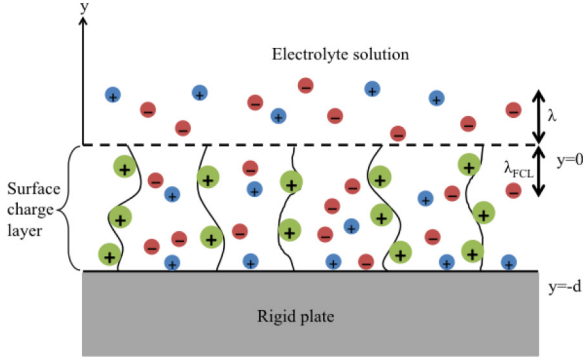


FIG. 1. (Color online) Schematic of the soft interface (consisting of a fixed charge layer or FCL and a rigid plate) in contact with an electrolyte solution. The FCL contains the electrolyte cations and anions as well as a third ion (shown in green), which is impermeable to the electrolyte. This third kind of ion has a valence  $Z$  and is distributed within the FCL with a uniform charge density  $N$ .

Despite such substantial research on the electrostatics of soft interfaces, remarkably most of these calculations typically invoke the mean field PB model. Therefore, several issues which are beyond the mean field description, such as consideration of finite ion sizes [9,11–14] or solvent polarization [8,9], etc., have remained elusive in the context of the electrostatics of soft interfaces. In this article, we provide a theory to analyze the influence of finite ion sizes (or steric effect) in the electrostatics of a soft interface in contact with an electrolyte solution. Our theory is based on a free energy model that appropriately accounts for the finite ion sizes as well as the geometric specifications of the soft interface (see Fig. 1). Our central result is that the Donnan potential ( $\psi_D$ ), which characterizes the electrostatic distribution of a soft interface with explicit consideration of selective ion permeability of the interface, increases in magnitude with an increase in the steric factor, with the extent of this variation being strongly dictated by the ratio of  $\lambda_{\text{FCL}}/\lambda$ . We provide analytical expressions justifying such an increase in the Donnan potential with finite ion size effects. This particular variation of  $\psi_D$  leads to a simultaneous depletion of both permeable electrolyte anions and cations from within the FCL—such steric-effect-mediated ion distribution will have remarkable implications in different applications involving a biomembrane, which is typically approximated as the ion-selective interface of the FCL and the adjacent electrolyte [25,37,38].

## II. THEORY

We start by considering a soft charged plate in contact with an electrolyte solution. Following the classical methodology for representing a charged soft plate [21–23], for our case too we assume that the soft plate is represented by a hard plate covered by a layer (of thickness  $d$ ) of ion-penetrable polyelectrolytes (which is the FCL that we have described above) (see Fig. 1). The free energy describing the above system can be expressed as

$$\mathcal{F} = \int f[\psi, n_{\pm}] d\mathbf{r}, \quad (1)$$

where  $f$  is the free energy density, expressed as

$$\begin{aligned} f = & -\frac{\epsilon_0 \epsilon_r}{2} |\nabla \psi|^2 + ez\psi(n_+ - n_-) + eZN\psi[\theta(y+d) \\ & - \theta(y)] + \frac{k_B T}{a^3} [n_+ a^3 \ln(n_+ a^3) + n_- a^3 \ln(n_- a^3) \\ & + (1 - n_+ a^3 - n_- a^3) \ln(1 - n_+ a^3 - n_- a^3)]. \end{aligned} \quad (2)$$

In Eq. (2),  $\epsilon_0$  is the permittivity of free space,  $\epsilon_r$  is the relative permittivity (assumed to be identical for both the FCL and the EDL),  $\psi$  is the electrostatic potential,  $n_{\pm}$  and  $\pm z$  are the ion number densities and valence of the electrolyte ions (these ions are present both within the FCL as well as the EDL),  $N$  and  $Z$  are the number density and valence of the particular kind of ion that is present only in the FCL (see the caption of Fig. 1),  $a$  is the parameter quantifying the ion size,  $k_B T$  is the thermal energy, and  $\theta$  is the Heaviside function. On the right hand side of Eq. (2), the first term represents the self-electrostatic energy of the FCL and the EDL, the second term represents the electrostatic energy of the electrolyte ions, the third term represents the electrostatic energy of the ions present only within the FCL, and the fourth term represents the energy due to mixing entropy of the ions. Such an expression of the free energy of the EDL electrostatics, accounting for the combined influences of the FCL (representing the “softness” of a soft surface) and finite ion size effect, is discussed in this article. In most previous studies either the free energy of the EDL electrostatics with a finite ion size effect for a rigid surface [11,13], or the electrostatic potential distribution of a soft surface with point sizes of ions [21–23] has been considered—Eq. (2) provides a framework that allows for simultaneous accounting of these effects. The equilibrium conditions are obtained by employing  $\delta \mathcal{F} / \delta \psi = 0$  and  $\delta \mathcal{F} / \delta n_{\pm}$ , which will yield

$$\begin{aligned} \frac{d^2 \psi}{dy^2} &= -\frac{ez(n_+ - n_-)}{\epsilon_0 \epsilon_r}, \quad y > 0 \\ \frac{d^2 \psi}{dy^2} &= -\frac{ez(n_+ - n_-) + ZeN}{\epsilon_0 \epsilon_r}, \quad -d < y < 0, \end{aligned} \quad (3)$$

and

$$n_{\pm} = \frac{n_{\infty}}{1 - 2\nu + 2\nu \cosh(ez\psi/k_B T)} \exp\left(\mp \frac{ez\psi}{k_B T}\right), \quad (4)$$

where  $\nu = n_{\infty} a^3$  is the steric factor ( $n_{\infty}$  being the bulk ionic number density). Using Eq. (4) in Eq. (3), we finally get the equation(s) dictating the electrostatic potential (in dimensionless form) as

$$\begin{aligned} \frac{d^2 \bar{\psi}}{d\bar{y}^2} &= \frac{\sinh(\bar{\psi})}{1 - 2\nu + 2\nu \cosh(\bar{\psi})}, \quad \bar{y} > 0, \\ \frac{d^2 \bar{\psi}}{d\bar{y}^2} &= \frac{\sinh(\bar{\psi})}{1 - 2\nu + 2\nu \cosh(\bar{\psi})} - \frac{1}{K_{\lambda}^2}, \quad -\bar{d} < \bar{y} < 0, \end{aligned} \quad (5)$$

where  $\bar{y} = \frac{y}{\lambda}$ ,  $\bar{\psi} = \frac{ez\psi}{k_B T}$ ,  $\bar{d} = \frac{d}{\lambda}$  (where  $\lambda = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{2n_{\infty} e^2 z^2}}$ ), and  $K_{\lambda} = \frac{\lambda_{\text{FCL}}}{\lambda}$  (where  $\lambda_{\text{FCL}} = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{Ne^2 z^2}}$ ). Please note that in our model we have considered identical values of the steric factor for both the FCL and the EDL, although we can easily modify the free energy expression [see Eq. (2)] to ensure that our model considers different values of steric factors for the FCL

and the EDL. We solve Eq. (5) numerically in the presence of the following dimensionless boundary conditions:

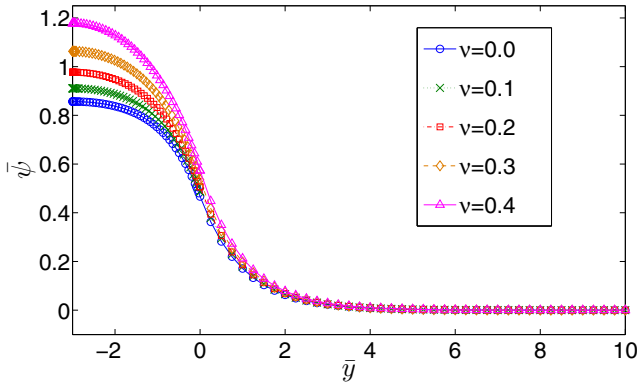
$$\begin{aligned} \left(\frac{d\bar{\psi}}{d\bar{y}}\right)_{\bar{y}=-\bar{d}} &= 0, \quad \bar{\psi}_{\bar{y}=0^+} = \bar{\psi}_{\bar{y}=0^-}, \\ \left(\frac{d\bar{\psi}}{d\bar{y}}\right)_{\bar{y}=0^+} &= \left(\frac{d\bar{\psi}}{d\bar{y}}\right)_{\bar{y}=0^-}, \quad \left(\frac{d\bar{\psi}}{d\bar{y}}\right)_{\bar{y}\rightarrow\infty} = 0. \end{aligned} \quad (6)$$

Before discussing the numerical results of the variation of the EDL electrostatics, we express the relationship governing the Donnan potential with the potential at the interface of the FCL and the bulk electrolyte, i.e., at  $y = 0$  (we shall henceforth call it  $\psi_0$ , which is also called the surface potential of soft surfaces [39]). Please note it is well established that for the case of no finite ion size effects, we necessarily have [23]

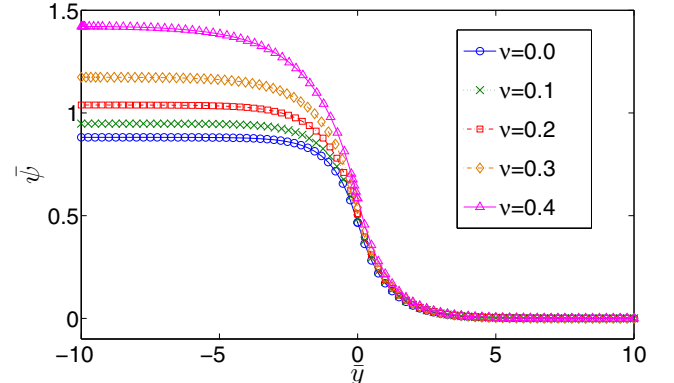
$$\bar{\psi}_D - \bar{\psi}_0 = \tanh\left(\frac{\bar{\psi}_D}{2}\right), \quad (7)$$

where  $\bar{\psi}_0 = ez\psi_0/k_B T$  and  $\bar{\psi}_D = ez\psi_D/k_B T$ . To obtain the corresponding relationship for the case of finite ion size effects, we shall first resort to express the charge neutrality at  $y = -d$ , so that (considering the case where  $d \gg \lambda$ , i.e.,  $\psi_{y=-d} = \psi_D$ )

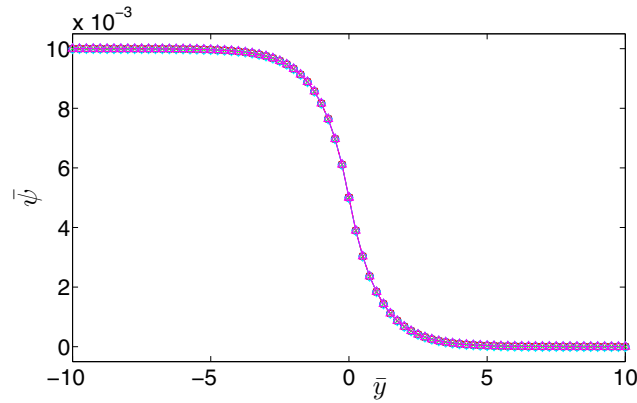
$$\begin{aligned} [NeZ + ez(n_+ - n_-)]_{y=-d} &= 0 \\ \Rightarrow NeZ &= \frac{2n_\infty ez \sinh(ez\psi_D/k_B T)}{1 - 2\nu + 2\nu \cosh(ez\psi_D/k_B T)}. \end{aligned} \quad (8)$$



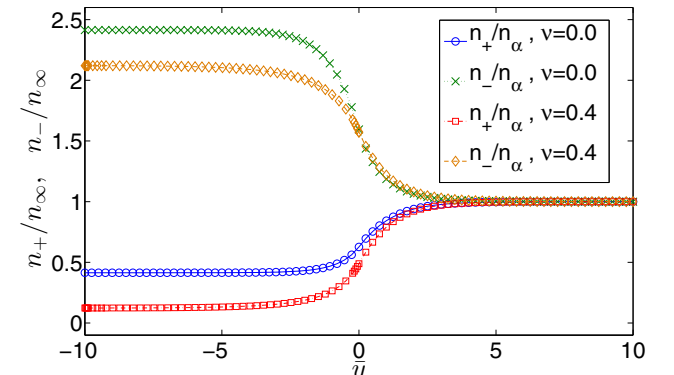
(a)



(b)



(c)



(d)

FIG. 2. (Color online) (a)–(c) Variation of the EDL potential reflecting the effect of finite ion sizes for (a)  $K_\lambda = 1$ ,  $\bar{d} = 3$ , (b)  $K_\lambda = 1$ ,  $\bar{d} = 10$ , and (c)  $K_\lambda = 10$ ,  $\bar{d} = 10$ . In (c), the electrostatic potential shows a negligible variation with the steric factor. For (b) and (c)  $\bar{d} = d/\lambda \gg 1$ , and hence the potential deep within the FCL (FCLs exist for  $\bar{y} < 0$ , whereas the electrolyte exists for  $\bar{y} > 0$ ; see Fig. 1) is the Donnan potential. (d) Variation of the ion number densities for different steric factors for  $\bar{d} = 10$  and  $K_\lambda = 1$ .

Plugging this relationship expressed in Eq. (8) into Eq. (3), and integrating the equations once and employing the appropriate boundary conditions, we shall finally get (in dimensionless form)

$$\begin{aligned} \frac{1}{2} \left(\frac{d\bar{\psi}}{d\bar{y}}\right)^2 &= \frac{1}{2\nu} \ln [1 - 2\nu + 2\nu \cosh(\bar{\psi})], \quad y > 0, \\ \frac{1}{2} \left(\frac{d\bar{\psi}}{d\bar{y}}\right)^2 &= \frac{1}{2\nu} \ln \left[ \frac{1 - 2\nu + 2\nu \cosh(\bar{\psi})}{1 - 2\nu + 2\nu \cosh(\bar{\psi}_D)} \right] \\ &\quad - \frac{\sinh(\bar{\psi}_D)}{1 - 2\nu + 2\nu \cosh(\bar{\psi}_D)} (\bar{\psi} - \bar{\psi}_D), \\ &\quad -\bar{d} < \bar{y} < 0. \end{aligned} \quad (9)$$

Equating the above two expressions at  $\bar{y} = 0$ , we shall finally get

$$\begin{aligned} \Rightarrow \bar{\psi}_D - \bar{\psi}_0 &= \left[ \frac{1 - 2\nu + 2\nu \cosh(\bar{\psi}_D)}{2\nu \sinh(\bar{\psi}_D)} \right] \\ &\quad \times \ln [1 - 2\nu + 2\nu \cosh(\bar{\psi}_D)]. \end{aligned} \quad (10)$$

Equation (10) provides the relationship between the dimensionless Donnan potential ( $\bar{\psi}_D$ ) and the surface potential ( $\bar{\psi}_0$ ) for the case where finite ion sizes are important. It can be easily seen that employing  $\nu \rightarrow 0$  in Eq. (10), we recover Eq. (7).

### III. RESULTS AND DISCUSSIONS

In Figs. 2(a)–2(c), we show the transverse variation of the electrostatic potential within the FCL and the EDL as a function of parameters such as the dimensionless FCL thickness  $\bar{d}$ , ratio  $K_\lambda$ , and the steric factor  $\nu$ . The central result of this article is the manner in which the variation in  $\nu$  affects the Donnan potential  $\psi_D$ . We find that an increase in  $\nu$  increases  $\psi_D$ . Below we justify this key finding from both mathematical and physical arguments. Equation (8) can be expressed in dimensionless form as

$$\frac{\sinh(\bar{\psi}_D)}{1 - 2\nu + 2\nu \cosh(\bar{\psi}_D)} = \frac{1}{K_\lambda^2}, \quad (11)$$

which can be solved to obtain (considering the positive root)

$$\bar{\psi}_D = \ln \left[ \frac{(1 - 2\nu) + \sqrt{(1 - 2\nu)^2 + (K_\lambda^4 - 4\nu^2)}}{(K_\lambda^2 - 2\nu)} \right]. \quad (12)$$

For  $K_\lambda = 1$ , we shall get from Eq. (12),  $\bar{\psi}_D = \ln [1 + \sqrt{2/(1 - 2\nu)}]$ , clearly justifying the enhancement of  $\bar{\psi}_D$  with an increase in  $\nu$  [see Figs. 2(a) and 2(b)]. Similarly, when  $K_\lambda \gg 1$ , Eq. (12) yields  $\bar{\psi}_D \approx \ln(1) \approx 0$ , explaining why  $\bar{\psi}_D$  is very small and independent of  $\nu$  [see Fig. 2(c)]. Please note that Eq. (12) fails to predict the behavior for the cases where  $K_\lambda \ll 1$ . Equation (12) can still provide a prediction for  $K_\lambda < 1$ , as long as the argument within the logarithm is positive [see Eq. (12)], and that prediction suggests that  $\bar{\psi}_D$  always increases with  $\nu$ . For the case when the FCL contains anions as fixed ions (we do not provide numerical results for this case), we get

$$\bar{\psi}_D = \ln \left[ \frac{-(1 - 2\nu) + \sqrt{(1 - 2\nu)^2 + (K_\lambda^4 - 4\nu^2)}}{(K_\lambda^2 + 2\nu)} \right]. \quad (13)$$

From Eq. (13), we get  $(\bar{\psi}_D)_{K_\lambda=1} = \ln \left[ \frac{\sqrt{2(1-2\nu)} - (1-2\nu)}{2\nu+1} \right]$ , so that as  $\nu$  increases,  $|\bar{\psi}_D|$  also increases. Further, from Eq. (13), we shall also get  $(\bar{\psi}_D)_{K_\lambda \gg 1} \approx 0$  (and hence independent of  $\nu$ ). We can also propose a physical explanation for such a dependence of  $\bar{\psi}_D$  on  $\nu$ . For the FCL at the point of electroneutrality (i.e., at the location where  $\psi = \psi_D$ ), the net electrolyte charge density must equal the value of the fixed charge. However, the finite ion size effect necessarily decreases the net electrolyte charge content across a given distance from a given charged surface [12]. Therefore, to ensure that, despite

this steric-effect-induced decrease, the net electrolyte charge content is still equal to this fixed charge, the magnitude of the corresponding potential (which is  $\psi_D$ ) must increase. This justifies why we expect that the magnitude of  $\psi_D$  must always increase with  $\nu$ .

In Fig. 2(d), we show the variation of the ion number densities as a function of the steric factor. Although the Donnan potential increases with the steric factor, the number densities of both the electrolyte cation and anion decrease. This decrease is such that the net difference remains identical, since the number density of the other ion (present exclusively within the FCL) remains constant. Physically, such a simultaneous lowering of both electrolyte cations and anions is similar to the widely known phenomenon of ion depletion due to the concentration polarization [7,40,41], although here the effect is triggered by merely the physical effects of the ions rather than any externally employed stimulus.

The Donnan potential of soft gels [e.g., the family of *polyacrylamide-co-sodium acrylate* [42] or *poly(N-isopropylacrylamid-co-carboxyacrylamid)* [43] gels] has been obtained by measuring the conductivities of these gels [42,43]. In order to validate the present theory, one can employ these well known techniques to obtain the gel conductivities (and hence the Donnan potential) for different concentrations of the electrolyte or different types of electrolyte ions (either of these factors will alter  $\nu = n_\infty a^3$ ).

### IV. CONCLUSIONS

To summarize, we have developed a theoretical model to study the effect of finite ion sizes in an EDL-mediated electrostatic distribution at the interface of a soft surface and an electrolyte solution. The model is a preliminary attempt to study soft matter electrostatics beyond the mean field description. The main result of the study establishes that finite ion sizes increase the magnitude of the Donnan potential, which is the central parameter in the study of soft matter electrostatics. As a consequence, there is an effect analogous to ion depletion in the concentration polarization—here the number densities of both the electrolyte cations and anions are lowered within the FCL. Such a steric-effect-triggered electrolyte ion depletion within the FCL, with the FCL-electrolyte interface being often conceived as a hypothetical biomembrane [25], would be extremely significant in context of different related events, such as the alteration in the conductivity of a biomembrane [44,45], regulation of osmotic pressure across a membrane [33,46], etc.

[1] R. J. Hunter, *Zeta Potential in Colloid Science* (Academic, London, 1981).  
 [2] J. Lyklema, *Fundamentals of Interface and Colloid Science* (Academic, San Diego, 1991).  
 [3] D. C. Grahame, *Anal. Chem.* **30**, 1736 (1958).  
 [4] P. Attard, *Adv. Chem. Phys.* **92**, 1 (1996).  
 [5] J. C. T. Eijkel and A. van den Berg, *Microfluid. Nanofluid.* **1**, 249 (2005).  
 [6] R. B. Schoch, J. Han, and P. Renaud, *Rev. Mod. Phys.* **80**, 839 (2008).

[7] S. Das, P. Dubsky, A. van den Berg, and J. C. T. Eijkel, *Phys. Rev. Lett.* **108**, 138101 (2012).  
 [8] S. Das, S. Chakraborty, and S. K. Mitra, *Phys. Rev. E* **85**, 051508 (2012).  
 [9] R. P. Mishra, S. Das, and S. K. Mitra, *J. Chem. Phys.* **138**, 114703 (2013).  
 [10] S. Das and S. Hardt, *Phys. Rev. E* **84**, 022502 (2011).  
 [11] S. Das, *Phys. Rev. E* **85**, 012502 (2012).  
 [12] S. Das and S. Chakraborty, *Phys. Rev. E* **84**, 012501 (2011).

- [13] M. S. Kilic, M. Z. Bazant, and A. Ajdari, *Phys. Rev. E* **75**, 021502 (2007).
- [14] M. Z. Bazant, M. S. Kilic, B. D. Storey, and A. Ajdari, *Adv. Colloid Interface Sci.* **152**, 48 (2009).
- [15] C. J. McClanahan and D. A. McQuarrie, *J. Electrochem. Soc.* **131**, 534 (1984).
- [16] O. Schnitzer and E. Yariv, *Phys. Fluids* **24**, 082005 (2012).
- [17] E. Yariv and A. M. J. Davis, *Phys. Fluids* **22**, 052006 (2010).
- [18] S. Das and S. Chakraborty, *Langmuir* **26**, 11589 (2010).
- [19] R. Qiao, *Langmuir* **22**, 7096 (2006).
- [20] S. Lin, Y. Cheng, J. Liu, and M. R. Wiesner, *Langmuir* **28**, 4178 (2012).
- [21] H. Ohshima, *Sci. Technol. Adv. Mater.* **10**, 063001 (2009).
- [22] H. Ohshima, *Soft Matter* **8**, 3511 (2012).
- [23] A. C. Barbati and B. J. Kirby, *Soft Matter* **8**, 10598 (2012).
- [24] H. Ohshima, *Theory of Colloid and Interfacial Electric Phenomena* (Elsevier/Academic, New York, 2006).
- [25] K. Makino and H. Ohshima, *Sci. Technol. Adv. Mater.* **12**, 023001 (2011).
- [26] A. T. Poortinga, R. Bos, W. Norde, and H. J. Busscher, *Surf. Sci. Rep.* **47**, 1 (2002).
- [27] A. J. de Kerchove and M. Elimelech, *Langmuir* **21**, 6462 (2005).
- [28] U. Freudenberg, R. Zimmermann, K. Schmidt, S. H. Behrens, and C. Werner, *J. Colloid Interface Sci.* **309**, 360 (2007).
- [29] H. Ohshima, *J. Colloid Interface Sci.* **268**, 429 (2003).
- [30] H. Ohshima, *J. Colloid Interface Sci.* **323**, 92 (2008).
- [31] H. Ohshima, *J. Colloid Interface Sci.* **323**, 313 (2008).
- [32] J. J. Lopez-Garcia, J. Hornoa, and C. Grosse, *J. Colloid Interface Sci.* **268**, 371 (2003).
- [33] K. Kontturi, L. Murtoimäki, and J. A. Manzanares, *Ionic Transport Processes: In Electrochemistry and Membrane Science* (Oxford University Press, Oxford, UK, 2008).
- [34] H. Ohshima, *Colloids Surf., A* **379**, 18 (2011).
- [35] H. Ohshima, *J. Phys. Chem. A* **116**, 6473 (2012).
- [36] H. Ohshima, *Curr. Opin. Colloid Interface Sci.* **18**, 73 (2013).
- [37] H. Ohshima and S. Ohki, *Biophys. J.* **47**, 673 (1985).
- [38] S. McLaughlin, *Annu. Rev. Biophys. Biophys. Chem.* **18**, 113 (1989).
- [39] S. S. Dukhin, R. Zimmermann, and C. Werner, *J. Colloid Interface Sci.* **274**, 309 (2004).
- [40] H. Strathmann, *J. Membr. Sci.* **9**, 121 (1981).
- [41] S. J. Kim, Y.-A. Song, and J. Han, *Chem. Soc. Rev.* **39**, 912 (2010).
- [42] L. P. Yezek, J. F. L. Duval, and H. P. van Leeuwen, *Langmuir* **21**, 6220 (2005).
- [43] R. Zimmermann, D. Kuckling, M. Kaufmann, C. Werner, and J. F. L. Duval, *Langmuir* **26**, 18169 (2010).
- [44] I. Casuso, L. Fumagalli, J. Samitier, E. Padros, L. Reggiani, V. Akimov, and G. Gomila, *Nanotechnology* **18**, 465503 (2007).
- [45] D. O. Mak and W. W. Webb, *Biophys. J.* **72**, 1153 (1997).
- [46] N. T. Hancock and T. Y. Cath, *Environ. Sci. Technol.* **43**, 6769 (2009).