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The Donnan model derived from microstructure

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Abstract

The ideal Donnan potential of an ionized polyelectrolyte medium is shown to be an approximate solution to a system of Poisson–Boltzmann (PB) equations for a periodic array of charged plates in an electrolyte bath. This result, derived using homogenization and scaling methods, demonstrates that the macrocontinuum, thermodynamic Donnan, and statistical mechanical PB models describe the same phenomenon: electrostatic repulsion between fixed-charged groups (albeit at different length scales). The Donnan approximation is accurate at low ionic strength (i.e., where the Debye length is much larger than the separation between charged plates), but is less faithful at physiologic and higher ionic strength. This work also provides a framework for relating theories of electrostatic repulsive interactions formulated at microscopic and macroscopic length scales.

Keywords: Donnan; Poisson–Boltzmann; Homogenization; Double-layer repulsion; Composite medium; Cartilage; Gel

1. Introduction

Electrostatic interactions among matrix-bound ionized charge groups strongly influence the behavior of colloids [1], polyelectrolyte molecules [2,3] and gels [4,5], and biological materials such as connective tissues [6,7] and muscle [8]. In this paper, we relate coarse- and fine-scale models of these interactions, based on the ideal macrocontinuum Donnan and microcontinuum Poisson–Boltzmann (PB) theories. Both models are used widely in physical, colloid, and electrochemistry.

Microcontinuum PB models, like the hexagonal [9] or cylindrical [10–12] unit-cell models of double-layer interaction, can furnish numerical or analytic expressions for the space-varying electrostatic potential, electrostatic stress, and ionic distributions between polyelectrolyte molecules, given the bath ionic strength and molecular surface charge density.

Macrocontinuum models, like the Donnan model, assume that the electrostatic potential and ionic concentration are uniform within the polyelectrolyte phase (in contrast to the microcontinuum models). The Donnan model can be used to derive analytic expressions for the electrostatic potential difference, osmotic (swelling) pressure, and mean ionic concentration within the polyelectrolyte phase, given bath ionic strength and

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matrix volume fixed-charge density. However, the ideal Donnan model, although simpler mathematically, lacks sufficient microstructural detail to predict swelling pressure adequately in some regimes. Specifically, it overestimates the electrostatic potential, and thus the osmotic swelling pressure in certain colloids at high ionic strength (the Hammarsten effect) [13], in cartilage, and in other highly charged tissues at physiologic ionic strength [7,12].

The Donnan model, an equilibrium thermodynamic description of charged media, is derived by requiring that the electrochemical potentials of the mobile ions within interstices of the charged medium and the external bath be equal. The macrocontinuum length scale is assumed to be much larger than the electrical Debye length and the dimensions of the polyelectrolyte molecules, and is consistent with a spatially uniform potential and ionic concentration within the polyelectrolyte phase.

The PB equation, a statistical thermodynamic description of a charged medium in an electrolyte, is derived by combining Poisson's equation of electroquasistatics and Boltzmann's equilibrium distribution of mobile ions. The microcontinuum length scale is assumed to be much smaller than the electrical Debye length and the

molecular dimensions of the polyelectrolyte, and is consistent with a space-varying potential and ionic concentration within the polyelectrolyte phase.

Despite the importance and pervasiveness of the Donnan model and PB equation, the connection between them has not been elucidated. This entails first representing the polyelectrolyte phase using the PB equation with boundary conditions, and then comparing the solution with that predicted by the Donnan model.

In this paper we show that the macrocontinuum Donnan model can be derived directly from a microcontinuum PB model of a composite medium, using homogenization and scaling methods. First, we review the ideal Donnan theory, deriving the well-known Donnan equation relating the electrostatic potential and ionic concentrations within the polyelectrolyte phase and external bath. We then present a system of microcontinuum PB equations and interfacial (boundary) conditions for a composite medium—a periodic array of charged lamina in an ionic solution, as depicted in Fig. 1—from which we derive a homogenized one-dimensional PB equation that predicts the (averaged) macroscopic electrical potential distribution. Using scaling methods, we simplify this homogenized equation

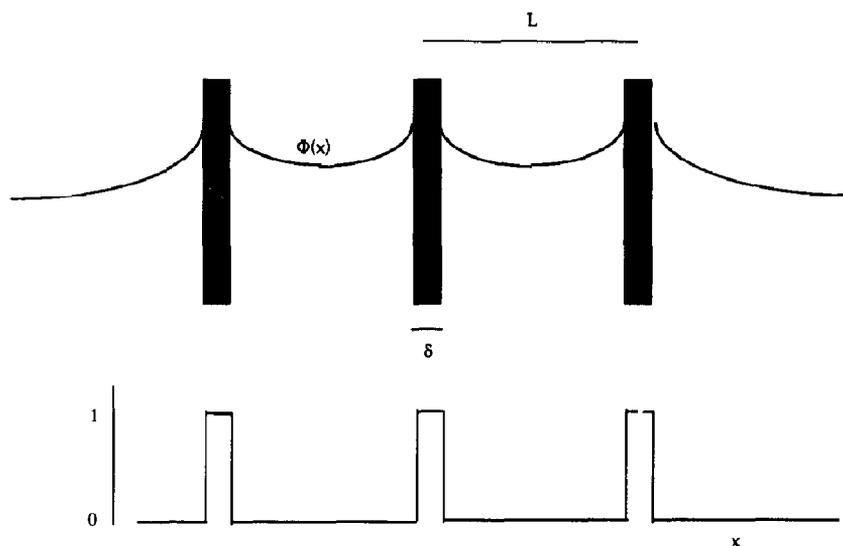


Fig. 1. Composite microcontinuum model of charged plates (above) and the indicator function, $\chi(x)$ (below).



Fig. 2. Macroscopic continuum model of charged medium having mean charge density ρ_m in a large reservoir, in which the salt concentration is c_b and the potential, Φ , is zero far from the charged medium.

further in order to compare its predictions to those of the Donnan model in low and high ionic strength regimes.

2. The Ideal Donnan model

Figure 2 shows a charged medium with its interstitial electrolyte communicating with an external bath. The ideal Donnan condition corresponds to the equality of the electrochemical potentials of the mobile ions in each phase. For an ideal polyelectrolyte and a monovalent salt electrolyte this Donnan condition is [13]:

$$\bar{c}^+ \bar{c}^- = c_b^2, \quad (1)$$

where c_b is the concentration of either positive or negative mobile ions in the external bath ($c^+ = c^- = c_b$), and \bar{c}^+ and \bar{c}^- are the concentrations of these ions in the polyelectrolyte phase.

The equality of electrochemical potentials of the mobile ions in each phase leads to an electrostatic potential difference. $\Delta\Phi_{\text{Donnan}}$ [13], between the polyelectrolyte phase and the bath:

$$\Delta\Phi_{\text{Donnan}} = -\frac{RT}{F} \ln\left(\frac{c_b}{\bar{c}^-}\right), \quad (2)$$

where $F = 96,487$ C/mol is Faraday's constant, $R = 8.314$ J/(mol K) is the ideal gas constant, and T is the absolute temperature in degrees Kelvin.

Bulk electroneutrality within the polyelectrolyte phase requires that

$$\frac{\rho_m}{F} + \bar{c}^+ - \bar{c}^- = 0, \quad (3)$$

where ρ_m is the mean density of fixed charges in

C/liter interstitial fluid. The relationship between the Donnan potential and the volume fixed charge density of the polyelectrolyte is found by solving eqs. (1)–(3) simultaneously:

$$\Delta\Phi_{\text{Donnan}} = \frac{RT}{F} \ln\left(\frac{\rho_m}{2Fc_b} + \sqrt{\left(\frac{\rho_m}{2Fc_b}\right)^2 + 1}\right). \quad (4)$$

3. The PB equation in each phase

Figure 1 shows an array of charged, impermeable plates, each being δ wide, spaced a distance L apart. A surface charge density on the plates, which is commonly used as a boundary condition for the PB equation in charged media [14], is here replaced by a uniform fixed-charge density ρ_f within the plate (C/liter-plate-volume). Thus, for simplicity, the matrix fixed charge is modeled as a localized volume density, rather than as a surface fixed-charge density. The interstitial electrolyte phase has a mobile charge density ρ_e , due to an unequal concentration of co- and counter-ions, which is a function of position. The interstitial electrolyte communicates with an external reservoir with ionic concentration c_b . The electrostatic potential is assumed to be zero in the external bath, several Debye lengths away from the charged plates. We treat the ions in the solvent as point charges; i.e., they have zero volume. Because of symmetry, the distribution of ions varies only in the x -direction, perpendicular to the interface. The dielectric permittivities of the space-charge region, the bulk solution, and the plates are assumed to be independent of electric field strength. There are no other charged species or impurities present.

Poisson's equation relates the potential, Φ_e , and charge distribution, ρ_e , within the interstitial electrolyte solution:

$$\nabla^2 \Phi_e = -\rho_e/\epsilon_e, \quad (5)$$

in which ϵ_e is the permittivity of the interstitial fluid. For an array of charged plates, the potential depends only on the coordinate perpendicu-

lar to the plane of the plates, x , so eq. (5) reduces to

$$\frac{\partial^2 \Phi_e}{\partial x^2} = -\frac{\rho_e}{\epsilon_e}. \quad (6)$$

The mobile charge density at each position is related to the ionic concentrations by

$$\rho_e(x) = F(\bar{c}^+(x) - \bar{c}^-(x)). \quad (7)$$

Locally, the system is in thermal equilibrium, in which only electrostatic and Brownian forces are acting on the electrolyte. Therefore, the probability of finding c_i at position x is given by the Boltzmann distribution [15]:

$$\bar{c}_i(x) = c_b \exp\left(\frac{-z_i F \Phi_e(x)}{RT}\right), \quad (8)$$

where once again c_b is the concentration of the electrolyte when $\Phi_e = 0$ far enough away from the charged medium, and z_i is the valence number. Combining eqs. (6–8) for a binary, monovalent electrolyte solution, we obtain

$$\frac{\partial^2 \Phi_e}{\partial x^2} = \frac{2Fc_b}{\epsilon_e} \sinh\left(\frac{F\Phi_e(x)}{RT}\right). \quad (9)$$

In addition, the potential distribution caused by fixed charges within the plates is also governed by Poisson's equation:

$$\frac{\partial^2 \Phi_f}{\partial x^2} = -\frac{\rho_f}{\epsilon_f}, \quad (10)$$

where ϵ_f is the permittivity of the plate. At the interface between a plate and the interstitial solution, the normal component of the displacement flux density, D , must be continuous, since we have assumed that the fixed charge is uniformly distributed within the plate. For a linear medium with no surface charge, the surface boundary condition corresponding to the continuity of displacement flux density is given by:

$$\epsilon_f E_{xf} - \epsilon_e E_{xe} = \sigma_{sn} = 0, \quad (11)$$

where σ_{sn} is the surface charge density and E_x is the electric field. For simplicity (but with no loss of generality), we now assume that the dielectric

permittivities are the same in both the solution and the fixed-charge media in eq. (11). The gradient of potential is therefore continuous at each boundary, i.e.,

$$\frac{\partial \Phi_e}{\partial x} = \frac{\partial \Phi_f}{\partial x}. \quad (12)$$

In addition, the electrical potential must also be continuous at a boundary; otherwise the electric field would be infinite. So,

$$\Phi_e = \Phi_f. \quad (13)$$

Equations (9) and (10) specify the microcontinuum PB equations in both domains, while eqs. (12) and (13) specify the conditions that must be satisfied at their interfaces.

4. The PB model for the composite medium

To derive the potential distribution in the medium, one might first write the appropriate PB equation in each domain with the interfacial jump conditions, then attempt to solve this system simultaneously. As a result, for an infinite medium, one would then have to solve an infinite number of simultaneous differential equations. A more prudent approach is to write the PB equation for the composite medium in a form that makes it amenable to simplification using homogenization methods:

$$\frac{\partial^2 \Phi}{\partial x^2} = (1 - \chi(x)) \frac{2Fc_b}{\epsilon} \sinh\left(\frac{F\Phi}{RT}\right) - \chi(x) \frac{\rho_f}{\epsilon}. \quad (14)$$

Above, $\Phi(x, t)$ is the potential throughout the composite medium with respect to the external bath that is assumed to be grounded. Information about the plate width and spacing is now contained in $\chi(x)$, a train of boxcar functions that are δ wide and spaced L apart, synthesized from unit Heaviside functions, $H(x)$, i.e.,

$$\chi(x) = \sum_{n=-\infty}^{n=+\infty} \left(H\left(x - nL + \frac{\delta}{2}\right) - H\left(x - nL - \frac{\delta}{2}\right) \right). \quad (15)$$

This indicator function, $\chi(x)$, shown in Fig. 2, is so defined as to be consistent with its use by Burridge and Keller [16]. Within the interior of the plate, $\chi(x) = 1$, so

$$\frac{\partial^2 \Phi}{\partial x^2} = -\frac{\rho_f}{\epsilon}; \quad (16)$$

within the ionic solution, $\chi(x) = 0$, so

$$\frac{\partial^2 \Phi}{\partial x^2} = \frac{2Fc_b}{\epsilon} \sinh\left(\frac{F\Phi}{RT}\right), \quad (17)$$

in agreement with eqs. (9) and (10) above.

The interfacial conditions, eqs. (12) and (13), also are implicit in eqs. (14) and (15). This can be seen by integrating eq. (14) across any solution/plate interface—for example, one at $x = x_0$. The continuity of the potential gradient can be shown by integrating eq. (14) once with respect to x :

$$\begin{aligned} \int_{x_0-\gamma}^{x_0+\gamma} \frac{\partial^2 \Phi}{\partial x^2} dx &= \frac{\partial \Phi(x_0 + \gamma)}{\partial x} - \frac{\partial \Phi(x_0 - \gamma)}{\partial x} \\ &= \int_{x_0-\gamma}^{x_0+\gamma} h(u) du. \end{aligned} \quad (18)$$

Above, γ is a small positive number, $h(x)$ is the right-hand side of eq. (14), and u is a dummy variable. It follows directly that the gradient of potential is continuous in the limit as γ approaches zero, since $h(x)$ is bounded¹ on the interval $(x_0 - \gamma < x < x_0 + \gamma)$, i.e.,

$$\begin{aligned} \lim_{\gamma \rightarrow 0} \left(\frac{\partial \Phi(x_0 + \gamma)}{\partial x} - \frac{\partial \Phi(x_0 - \gamma)}{\partial x} \right) \\ = \lim_{\gamma \rightarrow 0} \int_{x_0-\gamma}^{x_0+\gamma} h(u) du = 0, \end{aligned} \quad (19)$$

thus demonstrating that eq. (14) implies continuity of the electric field at the interface,

$$\frac{\partial \Phi(x_0^+)}{\partial x} = \frac{\partial \Phi(x_0^-)}{\partial x}. \quad (20)$$

¹ The boundedness of $h(x)$ is an Ansatz of the two-space method, but in this case it is easy to justify on physical grounds. The function $h(x)$ is the right hand side of eq. (14), which is just the charge density. Requiring that the charge density be finite is tantamount to requiring that the electric field be nowhere infinite in the medium.

By integrating eq. (14) with respect to x , we obtain:

$$\frac{\partial \Phi(x_0 + x)}{\partial x} = \frac{\partial \Phi(x_0 - \gamma)}{\partial x} + \int_{x_0-\gamma}^{x_0+x} h(u) du. \quad (21)$$

Integrating again between the limits $-\beta$ and β (where β is another small positive number),

$$\begin{aligned} \Phi(x_0 + \beta) - \Phi(x_0 - \beta) \\ = \frac{\partial \Phi(x_0 - \gamma)}{\partial x} (2\beta) + \int_{-\beta}^{\beta} \int_{x_0-\gamma}^{x_0+x} h(u) du dx. \end{aligned} \quad (22)$$

Taking the limit as γ and β approach zero,

$$\begin{aligned} \lim_{\beta \rightarrow 0} \lim_{\gamma \rightarrow 0} (\Phi(x_0 + \beta) - \Phi(x_0 - \beta)) \\ = \lim_{\beta \rightarrow 0} \lim_{\gamma \rightarrow 0} \left(\frac{\partial \Phi(x_0 - \gamma)}{\partial x} (2\beta) \right. \\ \left. + \int_{-\beta}^{\beta} \int_{x_0-\gamma}^{x_0+z} h(u) du dz \right); \end{aligned} \quad (23)$$

both terms on the right-hand side of eq. (23) must vanish. Therefore,

$$\Phi(x_0^+) = \Phi(x_0^-), \quad (24)$$

showing that eq. (14) also implies continuity of the potential at an interface. Therefore, eq. (14) is the PB model for the composite medium.

5. Deriving a homogenized PB equation

Homogenization methods are mathematical procedures that are used to simplify complicated governing equations by averaging them. While they have been used widely in continuum mechanics, to our knowledge they have not been applied in physical chemistry and colloid sciences. The method employed here to homogenize the composite PB model, eqs. (14) and (15), is based upon the two-space method [17–20].

Two spatial variables are identified: x' , which describes variations in potential on the order of the spacing between plates— $O(L)$; and $y(x') =$

x'/α , which changes more rapidly than x' and describes smaller scale variations on the order of the plate thickness— $O(\delta)$. We introduce a small perturbation parameter, $\alpha \sim O(\delta/L)$. The potential is assumed to depend upon both length scales; therefore, eqs. (14) and (15) can be rewritten as:

$$\frac{\partial^2 \Phi\left(x', \frac{x'}{\alpha}\right)}{\partial x'^2} = h\left(x', \frac{x'}{\alpha}\right) = h(x', y(x')), \quad (25)$$

where once again $h(x, y(x'))$ is the right-hand side of eq. (14). Since the potential depends upon both x' and $y(x')$, the chain rule requires that the partial differentiation operator with respect to x' be replaced by the following operator in x' and y :

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial x'} + \frac{1}{\alpha} \frac{\partial}{\partial y}. \quad (26)$$

Therefore, eq. (25) above becomes:

$$\left(\frac{\partial^2}{\partial x'^2} + \frac{2}{\alpha} \frac{\partial}{\partial y} \frac{\partial}{\partial x'} + \frac{1}{\alpha^2} \frac{\partial^2}{\partial y^2} \right) \Phi(x', y) = h(x', y). \quad (27)$$

The potential is now expanded as a power series in the perturbation parameter, α :

$$\begin{aligned} \Phi(x', y, \alpha) = & \Phi_0(x', y) + \Phi_1(x', y)\alpha \\ & + \Phi_2(x', y)\alpha^2 + O(\alpha^3) + \dots \end{aligned} \quad (28a)$$

Each function $\Phi_i(x', y)$ is assumed to be bounded. Similarly, we expand the right-hand side of eq. (14) using the same perturbation expansion:

$$\begin{aligned} h(x', y, \alpha) = & h_0(x', y) + h_1(x', y)\alpha \\ & + h_2(x', y)\alpha^2 + O(\alpha^3) + \dots \end{aligned} \quad (28b)$$

Substituting eqs. (28a,b) into eq. (27) and grouping terms with like powers of α , we get:

$$\alpha^{-2}: \frac{\partial^2 \Phi_0(x', y)}{\partial y^2} = 0, \quad (29a)$$

$$\alpha^{-1}: \frac{\partial}{\partial y} \frac{\partial \Phi_0(x', y)}{\partial x'} + \frac{\partial^2 \Phi_1(x', y)}{\partial y^2} = 0, \quad (29b)$$

and

$$\begin{aligned} \alpha^0: \frac{\partial^2 \Phi_0(x', y)}{\partial x'^2} + 2 \frac{\partial}{\partial y} \frac{\partial \Phi_1(x', y)}{\partial x'} \\ + \frac{\partial^2 \Phi_2(x', y)}{\partial y^2} = h_0(x', y). \end{aligned} \quad (29c)$$

Integrating the α^{-2} equation, eq. (29a), twice over the interval between y_0 and y , we obtain:

$$\begin{aligned} \Phi_0(x', y) = & \Phi_0(x', y_0) + (y - y_0) \\ & \times \left. \frac{\partial \Phi_0(x', y)}{\partial y} \right|_{y=y_0}, \end{aligned} \quad (30)$$

where y_0 is an arbitrary constant of integration. Since Φ_0 is bounded for all values of y , including the limit as y approaches infinity, the second term on the right-hand side of eq. (30) vanishes. Therefore,

$$\left. \frac{\partial \Phi_0(x', y)}{\partial y} \right|_{y=y_0} = 0 \quad (31)$$

for any y_0 , which implies that

$$\Phi_0(x', y) = \Phi_0(x'). \quad (32)$$

Physically, this means that the zeroth-order solution to the electrostatic potential varies on a macroscopic length scale. Moreover, eq. (32) simplifies the α^{-1} equation, eq. (29b), so that integrating it with respect to y yields:

$$\begin{aligned} \Phi_1(x', y) = & \Phi_1(x', y_0) + (y - y_0) \\ & \times \left. \frac{\partial \Phi_1(x', y)}{\partial y} \right|_{y=y_0}. \end{aligned} \quad (33)$$

In order for $\Phi_1(x', y)$ to be bounded,

$$\left. \frac{\partial \Phi_1(x', y)}{\partial y} \right|_{y=y_0} = 0 \quad (34)$$

so that

$$\Phi_1(x', y) = \Phi_1(x'). \quad (35)$$

Finally, integrating eq. (29c) with respect to y , using eqs. (32) and (35),

$$\begin{aligned} & \frac{1}{y-y_0} \frac{\partial \Phi_2(x', y)}{\partial y} \Big|_{y_0}^y \\ &= -\frac{d^2 \Phi_0(x')}{dx'^2} + \frac{1}{y-y_0} \int_{y_0}^y h_0(x', u) du, \end{aligned} \quad (36)$$

where u is a dummy variable. The term on the left-hand side of eq. (36) is continuous and bounded ($\partial \Phi_2(x', y)/\partial y$ is bounded because the electric field is finite). Therefore, in the limit as $y \rightarrow \infty$, the equation for the lowest order term in the perturbation expansion, eq. (29a–c), is given by:

$$\begin{aligned} \frac{d^2 \Phi_0(x')}{dx'^2} &= \lim_{y \rightarrow \infty} \frac{1}{y-y_0} \int_{y_0}^y h_0(x', u) du \\ &= \langle h_0(x') \rangle. \end{aligned} \quad (37)$$

This integral is an average of $h_0(x', y)$ over y , but it no longer explicitly depends upon this small-scale variable. This is the desired simplification: small-scale variations in potential have been eliminated by integration, but their macroscopic effect is preserved.

We perform the integration called for in eq. (37), using the result that

$$\begin{aligned} & \sinh\left(\frac{F\Phi(x', y, \alpha)}{RT}\right) \\ &= \sinh\left(\frac{F\Phi_0(x')}{RT}\right) + O(\alpha), \end{aligned} \quad (38)$$

so that $h(x', y)$ in eqs. (14) and (15) becomes

$$\begin{aligned} h(x', y) &= (1-\chi) \frac{2Fc_b}{\epsilon} \sinh\left(\frac{F\Phi_0(x')}{RT}\right) \\ &\quad - \chi \frac{\rho_f}{\epsilon} + O(\alpha). \end{aligned} \quad (39)$$

With no loss of generality, χ is now written as a function of y :

$$\begin{aligned} \chi(y) &= \sum_{n=-\infty}^{n=+\infty} \left[H\left(\alpha y - nL + \frac{\delta}{2}\right) \right. \\ &\quad \left. - H\left(\alpha y - nL - \frac{\delta}{2}\right) \right]. \end{aligned} \quad (40)$$

This form of χ guarantees that $h(x', y)$ will be continuously differentiable with respect to x' [16–18]. Because $\chi(y)$ has a period L/α in eq. (40), $\langle h(x') \rangle$ reduces to:

$$\langle h(x') \rangle = \frac{\alpha}{L} \int_{-L/2\alpha}^{L/2\alpha} h(x', u) du, \quad (41)$$

producing a forced PB equation for $\Phi_0(x')$:

$$\begin{aligned} \frac{d^2 \Phi_0(x')}{dx'^2} &= \left(1 - \frac{\delta}{L}\right) \frac{2Fc_b}{\epsilon} \sinh\left(\frac{F\Phi_0(x')}{RT}\right) \\ &\quad - \frac{\delta}{L} \frac{\rho_f}{\epsilon}. \end{aligned} \quad (42)$$

Equation (42) is simplified by scaling the potential by the thermal voltage:

$$\phi_0(x') = \frac{F\Phi_0(x')}{RT}, \quad (43)$$

from which we obtain

$$\begin{aligned} \frac{d^2 \phi_0(x')}{dx'^2} &= \left(1 - \frac{\delta}{L}\right) \frac{2F^2c_b}{RT\epsilon} \sinh(\phi_0(x')) \\ &\quad - \frac{\delta}{L} \frac{F\rho_f}{RT\epsilon}. \end{aligned} \quad (44)$$

Substituting the definition of the Debye length, $1/\kappa$,

$$\frac{2F^2c_b}{RT\epsilon} = \kappa^2, \quad (45)$$

which is the space constant of the electrostatic field between adjacent plates, we obtain the equation that the zeroth-order perturbation function must satisfy:

$$\frac{d^2 \phi_0(x')}{dx'^2} = \left(1 - \frac{\delta}{L}\right) \kappa^2 \sinh(\phi_0(x')) - \frac{\delta}{L} \frac{F\rho_f}{RT\epsilon}. \quad (46)$$

Homogenization redistributes the charge in the plate and ionic solution uniformly over the medium, but weighs them according to their respective volume fractions. Heuristically, we understand eq. (46) by treating the composite medium as both random and nonperiodic. The indicator function χ becomes a random variable,

and eq. (14) is a stochastic differential equation. Taking either an ensemble or volumetric average of eq. (14), and noting that

$$\langle(1-x)\rangle = \left(1 - \frac{\delta}{L}\right) \quad \text{and} \quad \langle x \rangle = \frac{\delta}{L}, \quad (47)$$

we produce a mean differential equation identical to eq. (46).

6. Deriving the Donnan potential from the homogenized PB model

Suppose the polyelectrolyte matrix is in equilibrium with an infinite reservoir in which the salt concentration is c_b and $\Phi_0 = 0$ far from the charged medium. Let us consider the general case in which the potential, ϕ , is observed on a macroscopic length scale, $W \gg L$, within the medium. For example, this case could represent a measurement of the potential within the charged medium using a glass microelectrode or a voltage-sensitive dye that has a finite resolution W , where $W \gg L$. Thus, we define a new nondimensional variable, x , by normalizing x' by its characteristic length W , i.e.,

$$x = \frac{x'}{W}. \quad (48)$$

Rescaling eq. (46) and using eq. (45), we obtain:

$$\left(\frac{1/\kappa}{W}\right)^2 \frac{d^2\phi_0(xW)}{dx^2} = \left(1 - \frac{\delta}{L}\right) \sinh(\phi_0(xW)) - \frac{\delta}{L} \frac{\rho_f}{2Fc_b}. \quad (49)$$

For a tissue like cartilage or a charged gel equilibrated at physiological ionic strength, both the Debye length, $1/\kappa$, and the intermolecular spacing, L , may be on the order of nanometers, while W may be on the order of micrometers to millimeters. Therefore, with $W \gg 1/\kappa$, we can ignore the spatial variation in ϕ_0 in eq. (49):

$$0 = \left(1 - \frac{\delta}{L}\right) \sinh(\phi_0(xW)) - \frac{\delta}{L} \frac{\rho_f}{2Fc_b}. \quad (50)$$

Equation (50) implies that ϕ_0 is a constant, i.e.,

$$\phi_0(xW) = \phi_0. \quad (51)$$

At equilibrium, no macroscopic potential variations are measurable at the resolution of this experiment, so that the electrical potential appears to be uniform, and the electric field appears to vanish within the charged medium. Using eq. (43), we can solve eq. (50) for Φ_0 :

$$\Phi_0 = \frac{RT}{F} \sinh^{-1} \left(\frac{\delta\rho_f}{(L-\delta)2Fc_b} \right). \quad (52)$$

Using a well-known identity, eq. (52) becomes:

$$\Phi_0 = \frac{RT}{F} \ln \left(\left(\frac{\delta\rho_f}{(L-\delta)2Fc_b} \right) + \sqrt{\left(\frac{\delta\rho_f}{(L-\delta)2Fc_b} \right)^2 + 1} \right), \quad (53)$$

which is identical to the ideal Donnan potential given in eq. (4) when

$$\rho_m = \frac{\delta\rho_f}{L-\delta}. \quad (54)$$

Recall that ρ_m is the average charge density obtained by dividing the total fixed charge by the fluid volume. Note that the right-hand side of eq. (54) is also the average fixed charge density, i.e., the total charge per plate divided by the electrolyte volume between plates. With this identification, the rescaled zeroth-order potential that solves the microcontinuum PB equation is the Donnan potential of a uniformly charged medium, eq. (4). This is the relationship we set out to establish.

The uniformity of electrical potential in the charged medium is an explicit assumption of the Donnan model that is seldom examined or challenged. Here we showed that $W \gg L$ is a necessary condition to satisfy this assumption. By contrast, when W is on the order of L , the electrical potential will vary spatially at the microscopic level.

7. Calculating higher order corrections to Φ in the PB micromodel

While we have established that the Donnan potential approximates the solution to the micro-continuum PB model, we have yet to assess the quality of the approximation it represents. To assess the accuracy of eq. (53), we should determine higher-order terms in the perturbation expansion of the potential, eq. (28a), and their relative contributions (or solve the PB model numerically). The homogenization method used above provides a means to calculate these terms, just as the activity coefficients are used to correct the Donnan condition when polyelectrolyte concentration is high [13]. We include below the equations for the first-order perturbation, to which we will refer when we consider the cases of low and high ionic strength limits of the PB model.

The equation for $\Phi_1(x')$ is obtained by re-grouping terms that share a common factor of α , i.e.,

$$\begin{aligned} & \frac{\partial^2 \Phi_3(x', y)}{\partial y^2} + \frac{\partial^2 \Phi_2(x', y)}{\partial x' \partial y} + \frac{d^2 \Phi_1(x')}{dx'^2} \\ &= \left(1 - \frac{\delta}{L}\right) \frac{2F^2 c_b \Phi_1(x')}{RT\epsilon} \cosh\left(\frac{F\Phi_0(x')}{RT}\right). \end{aligned} \quad (55)$$

Therefore, using the definition of the Debye length, we obtain

$$\begin{aligned} & \frac{\partial^2 \Phi_3(x', y)}{\partial y^2} + \frac{\partial^2 \Phi_2(x', y)}{\partial x' \partial y} + \frac{d^2 \Phi_1(x')}{dx'^2} \\ &= \left(1 - \frac{\delta}{L}\right) \kappa^2 \cosh\left(\frac{F\Phi_0(x')}{RT}\right) \Phi_1(x'). \end{aligned} \quad (56)$$

Integrating this equation with respect to y , we obtain:

$$\begin{aligned} & \frac{\partial \Phi_3(x', y)}{\partial y} + \frac{\partial \Phi_2(x', y)}{\partial x'} \\ &= \left\{ -\frac{d^2 \Phi_1(x')}{dx'^2} + \left(1 - \frac{\delta}{L}\right) \kappa^2 \right. \\ & \quad \left. \times \cosh\left(\frac{F\Phi_0(x')}{RT}\right) \Phi_1(x') \right\} (y - y_0). \end{aligned} \quad (57)$$

In the limit as $y \rightarrow \infty$, we see that the expression in braces on the right-hand side must vanish because of the physical assumptions of boundedness of $\Phi_3(x', y)$ and $\Phi_2(x', y)$; therefore,

$$\begin{aligned} & \frac{d^2 \Phi_1(x')}{dx'^2} = \left(1 - \frac{\delta}{L}\right) \kappa^2 \\ & \quad \times \cosh\left(\frac{F\Phi_0(x')}{RT}\right) \Phi_1(x'). \end{aligned} \quad (58)$$

In principle, by substituting an expression for $\Phi_0(x')$ into eq. (58), and applying appropriate boundary conditions, we could solve for $\Phi_1(x')$. However, we have not found a general analytical expression for $\Phi_0(x')$, so we would have to determine higher order corrections numerically. Even so, we can consider eq. (58) in the limiting cases of “high” and “low” ionic strength, and thus determine the first-order correction to Φ for the composite PB model.

8. Comparison between the PB and Donnan models at “low” ionic strength

Within the context of the Donnan and PB models, high and low ionic strength are relative terms. Low ionic strength corresponds to the Debye length being larger than the separation between plates, i.e., $1/\kappa \gg L$. Consider again that the charged matrix is in equilibrium with the infinite reservoir, in which the salt concentration is c_b and $\Phi_0 = 0$ far from the charged medium. With the condition $1/\kappa > L > \delta$, we now choose L as our characteristic length, and redefine the nondimensional variable, x , so that:

$$x = x'/L. \quad (59)$$

Normalizing Φ_0 as in eq. (43), eq. (46) then becomes:

$$\begin{aligned} & \frac{d^2 \phi_0(xL)}{dx^2} = \left(\frac{L}{1/\kappa}\right)^2 \left[\left(1 - \frac{\delta}{L}\right) \right. \\ & \quad \left. \times \sinh(\phi_0(xL)) - \frac{\delta}{L} \frac{\rho_t}{2Fc_b} \right]. \end{aligned} \quad (60)$$

Because, by assumption, $(L\kappa)^2 \ll 1$, the right-hand side of eq. (60) is close to zero. Therefore, we can obtain an approximate solution to eq. (60) using perturbation methods. As in eq. (28a), we can expand $\phi_0(xL)$ as a power series of the perturbation parameter $\gamma = (L\kappa)^2$

$$\phi_0(xL, \gamma) = f_0(x) + f_1(x)\gamma + f_2(x)\gamma^2 + \dots, \quad (61)$$

where the $f_i(x)$ are bounded functions. We then substitute eq. (61) into eq. (60), use eq. (38), and collect terms in like powers of γ :

$$\gamma^0: \frac{d^2 f_0(x)}{dx^2} = 0, \quad (62a)$$

and

$$\gamma^1: \frac{d^2 f_1(x)}{dx^2} = \left(\left(1 - \frac{\delta}{L} \right) \sinh(f_0(x)) - \frac{\delta}{L} \frac{\rho_f}{2Fc_b} \right), \quad (62b)$$

The solution to the γ equation is $f_0(x) = ax + \phi_0$. Either symmetry (i.e., $f_0(x) = f_0(-x)$) or by the boundedness of $f_i(x)$, we see that $f_0(x) = \phi_0$. To determine ϕ_0 , we substitute $f_0(x) = \phi_0$ into eq. (62b):

$$\gamma^1: \frac{d^2 f_1(x)}{dx^2} = \left(\left(1 - \frac{\delta}{L} \right) \sinh(\phi_0) - \frac{\delta}{L} \frac{\rho_f}{2Fc_b} \right), \quad (63b)$$

the right-hand side of which is now constant. Integrating (63b) two times with respect to x , we obtain the solution $f_1(x) = qx^2/2 + rx + s$. Again, by the boundedness of $f_1(x)$, we require that $q = r = 0$, so that

$$\frac{d^2 f_1(x)}{dx^2} = 0 = \left(\left(1 - \frac{\delta}{L} \right) \sinh(\phi_0) - \frac{\delta}{L} \frac{\rho_f}{2Fc_b} \right). \quad (64)$$

Equation (64) again implies that ϕ_0 is given by the Donnan equation (far from the boundary layer at the interface of the bath and the charged

medium); at low ionic strength. Therefore, we are left with:

$$\Phi_0 = \frac{RT}{F} \ln \left(\left(\frac{\delta \rho_f}{(L - \delta) 2Fc_b} \right) + \sqrt{\left(\frac{\delta \rho_f}{(L - \delta) 2Fc_b} \right)^2 + 1} \right) + O \left(\left(\frac{L}{1/\kappa} \right)^2 \right). \quad (65)$$

By symmetry, the solution of eq. (58) is $\Phi_1(x) = 0$. Therefore the Donnan approximation is accurate to $O(\alpha^2)$, i.e., $\Phi(x) \approx \Phi_0 + O(\alpha^2)$. This result agrees qualitatively with that of Buschmann [12], who showed that both the Donnan theory and PB unit-cell models accurately predict potential difference in proteoglycan solutions at low ionic strength. Intuitively, when $((1/\kappa L)^2 \gg 1)$, the potential between the plates predicted by a PB unit cell model is nearly uniform, so that the assumption of uniform potential implicit in the Donnan model is satisfied.

9. Comparison between the PB and Donnan models at high ionic strength

In the Donnan and PB models, high ionic strength corresponds to the Debye length being smaller than the separation between plates, i.e., $1/\kappa < L$. This is the case for cartilage and other tissues under physiological conditions [7]. One serious deficiency of the Donnan model is that it overestimates the mean potential in this regime [7,12]. Under the conditions, $L > 1/\kappa > \delta$, the potential will vary between plates. Scaling arguments can no longer be used to simplify the homogenized PB equations. Instead, the full differential equations for each term in the perturbation expansion of Φ must be solved, although it is possible to use higher order terms in the perturbation expansion of Φ to extend the range of applicability of the Donnan model. Since eq. (46) has no analytic solution, these corrections must be determined numerically, which we have not attempted to do in this paper.

10. Concluding remarks

Equation (53), derived using homogenization and scaling methods, demonstrates that the macrocontinuum, thermodynamic Donnan, and statistical mechanical PB models describe the same phenomenon: electrostatic repulsion between fixed-charged groups (albeit at different length scales).

Further, we have shown that Φ predicted by the ideal Donnan is an approximation to Φ calculated using a composite PB model.

For a physiologic or high ionic strength bath, we have shown that the ideal Donnan Φ is not guaranteed to be accurate to more than $O(\alpha)$. However, for a low ionic strength bath, the Donnan Φ is in excellent agreement with Φ predicted for the composite PB model, and is accurate to $O(\alpha^2)$.

Homogenization methods, like the averaging procedure presented above, provide a bridge between the micro- and macrocontinuum domains, often leading to simple macroscopic governing equation that retains microstructural and microscopic information [16]. These perturbation and scaling techniques are particularly useful in analyzing systems of colloids, gels, and polyelectrolytes in which the molecular length scale δ , the separation between molecules, L , and the resolution of a measurement, W (or the electrical space constant, $1/\kappa$) differ from one another by several orders of magnitude.

In principle, this homogenization technique can be extended to two- and three-dimensional models of electrostatic repulsion between charged cylinders, spheres, cubes, and even media in which fixed charges are randomly distributed within an electrolyte phase. Burrige and Keller [16] were able to extend their one-dimensional two-space method [17,18] to three dimensions with little difficulty. By analogy with their work, we expect that a three-dimensional model of electrostatic repulsion will behave qualitatively like our one-dimensional model, and that the extension to three dimensions will be straightforward. Finally, we foresee using this homogenization method to calculate corrections to the Donnan potential in high and low salt regimes.

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Nomenclature

x	thickness coordinate, m
δ	width of plate, m
L	separation between plates, m
$\chi(x)$	indicator function, dimensionless
$\Phi(x)$	electrical potential of the composite, V
$\Phi_f(x)$	electrical potential within the plate, V
$\Phi_e(x)$	electrical potential within the electrolyte, V
$E_f(x)$	electric field within the plate, V/m
$E_e(x)$	electric field within the electrolyte, V/m
z	valence number, dimensionless
F	Faraday constant, 96,487 C/mol
R	universal gas constant, 8,314 J/mol K
T	absolute temperature, K
ϵ	dielectric permittivity of electrolyte and plate, F/m
ϵ_f	dielectric permittivity of plate, F/m
ϵ_e	dielectric permittivity of electrolyte, F/m
$\rho_c(x)$	free charge density in the electrolyte, mol/L interstitial fluid
ρ_f	fixed charge density in the plate, mol/L plate volume
ρ_m	average fixed charge density, mol/L interstitial fluid
c_b	concentration of salt in electrolyte bath, mol/L
c^+	positive ion concentration in bath, mol/L
c^-	negative ion concentration in bath, mol/L
$\overline{c^+}$	positive ion concentration in charged phase, mol/L
$\overline{c^-}$	negative ion concentration in charged phase, mol/L

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