

Upscaling the Poisson–Nernst–Planck equations for ion transport in weakly heterogeneous charged porous media

Václav Klika^a, Eamonn A. Gaffney^{b,*}

^a Czech Technical University in Prague, Department of Mathematics, FNSPE, Trojanova 13, Prague, 120 00, Czech Republic

^b University of Oxford, Wolfson Centre for Mathematical Biology, Mathematical Institute, Andrew Wiles Building, Radcliffe Observatory Quarter, Woodstock Road, Oxford, OX2 6GG, United Kingdom

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ABSTRACT

The Poisson–Nernst–Planck (PNP) equations govern the continuum level description of ions in electrolytes and especially the impact of charged surfaces. In numerous applications such surfaces are complex, varying on a small lengthscale compared to the overall scale of the system, often prohibiting the direct prediction of the osmotic swelling pressures induced by ion behaviours in Debye layers near surfaces. With periodicity, upscaling techniques can be readily used to determine the behaviour of the swelling pressure on large lengthscales without solving the PNP equations on the complex domain, though generalising to cases where the periodicity is only approximate is more challenging. Here, we generalise a method by Bruna and Chapman (2015) for upscaling a non-periodic diffusion equation to the PNP equations. After upscaling, we find a rational derivation of the swelling pressure closely resembling the classical, though phenomenological, use of Donnan membrane theory predictions for the swelling pressure in cartilage, together with a novel contribution driven by heterogeneous fixed (surface) charges. The resulting macroscale model is also shown to be thermodynamically consistent, though its comparison with a recent upscaled models for swelling pressure in cartilage mechanics emphasises the need to understand how macroscale models depend on differing upscaling techniques, especially in the absence of perfect periodicity.

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1. Introduction

The Poisson–Nernst–Planck (PNP) equations are the nonlinear mean-field equations for the dynamics of charged particles in electrolytes, and of particular importance in analysing the interplay between bulk and surface fixed charge [1], with numerous applications such as modelling particle separation technologies [2]. In many scenarios the surfaces are complex, with extensive variation on a small lengthscale, yet the impact of the charge distribution is only required at a larger scale. Given the periodicity on the microscale, multiple

* Corresponding author.

E-mail addresses: vaclav.klika@cvut.cz (V. Klika), gaffney@maths.ox.ac.uk (E.A. Gaffney).

scale asymptotics or homogenisation techniques, such as volume averaging, can be used to upscale from microscale dynamics to macroscale models without the need to solve the underlying equations on the complex domain [2–4]. However, the resultant macroscale models can differ with the details of the upscaling technique, while more generally an understanding of the relationship between the emergent macroscale model, the technique used for its derivation and the underlying microscale is underdeveloped [5]. Numerous applications of the PNP equations may also be found in modelling biological tissue, such as the swelling pressure generated by fixed surface charge in cartilage [6,7] and the influence of ion and ion channel dynamics on tissue level cardiac electrophysiology [8,9]. However, biological tissues often do not exhibit perfect periodicity on larger scales, hence the need for upscaling the PNP equations with methods that can accommodate an element of heterogeneity. Thus our objective is to use the homogenisation framework of Bruna et al. previously applied to a linear diffusion equation in an almost periodic domain with slow spatial variation [10], to upscale the PNP equations to determine macroscale swelling pressures in a weakly heterogeneous porous medium, with a charged solid phase and an electrolytic fluid phase. We will also compare the resulting macroscale model to both classical macroscale phenomenology for swelling pressure, based on Donnan membrane theory, and recent alternative approaches to upscaling the PNP equations with weak heterogeneity [7]. Finally, the thermodynamic consistency of the upscaling is considered by examining the force–flux relations and the fluctuation–dissipation theorem.

2. Derivation of the upscaled model

Nernst–Planck equations describe ion transport with a single thermodynamic force for each ion species, the electrochemical potential which acts on the microscale. The Poisson equation is a relation between the electric potential and the concentrations of ions following Maxwell’s electrostatic equations. The impracticality of carrying this detailed description through to macroscales lies in the details of the geometries on the microscale that, however, carry charge and thus are fundamental. We aim to circumvent this issue by upscaling to macroscale.

With V^f , V^s denoting fluid and solid phases of the porous medium, the Poisson–Nernst–Planck (PNP) equations for the concentration of a single positively charged ion, c^+ , and negatively charged ion, c^- , are

$$\partial_t c^\pm = \nabla_\xi \cdot \left[D^\pm \left(\nabla_\xi c^\pm + z^\pm c^\pm \frac{F}{RT} \nabla_\xi \phi \right) \right] \text{ in } V^f, \quad -\nabla_\xi \cdot (\epsilon(\xi) \nabla_\xi \phi) = F(z^+ c^+ + z^- c^-) \text{ in } V^f \cup V^s. \quad (1)$$

Here, ϕ [V] represents the electric potential, F [C/mol] the Faraday constant, R the gas constant, T [K] the absolute temperature, D^\pm [m²/s] the ion diffusion coefficients, z^\pm [1] the ion valences and ϵ [C/(V m)] the electric permittivity of the system, which typically differs between the solid and fluid phases. Note that the right-hand side of the Poisson equation for ϕ in Eq. (1) is nonzero only in V^f , with ξ [m] representing the dimensional spatial coordinate and its associated unit of metres [m]. We simplify by assuming that the ions have equal diffusion coefficients, $D^+ = D^- = D$, though different diffusion coefficients are readily reinstated below.

The equations are supplemented by boundary conditions, with no flux of ions from the fluid region and jump conditions for the electric potential ϕ corresponding to a finite electric field, and thus no jump in the potential, and a fixed charge density Q at the fluid–solid interface $\tilde{I} = \partial V^f \cap \partial V^s$. Hence,

$$\boldsymbol{\nu} \cdot \left[D^\pm \left(\nabla_\xi c^\pm + z^\pm c^\pm \frac{F}{RT} \nabla_\xi \phi \right) \right] = 0 \text{ at } \tilde{I}, \quad -[\epsilon(\xi) \boldsymbol{\nu} \cdot \nabla_\xi \phi] = Q, \quad [\phi] = 0 \quad \text{at } \tilde{I}, \quad (2)$$

where $\boldsymbol{\nu}$ denotes the outer unit normal to the *fluid* domain V^f and $[[u]]$ denotes the jump in values of a quantity u in the normal direction to the interface (positive if values in the fluid V^f are larger than in the solid V^s). We also consider the cell and its boundaries below, respectively denoted \mathcal{C} and $\partial\mathcal{C}$, assuming

the tissue is made up of cells that are periodic, except possibly for a long lengthscale drift of the cell properties. Finally, from the balance of forces, we obtain a relation for the swelling pressure p^{sw} in terms of ion concentration and electric potential via Lorentz force

$$-\nabla_{\xi} p^{sw} = F(z^+ c^+ + z^- c^-) \nabla_{\xi} \phi. \quad (3)$$

2.1. Multiscale expansion

First, we introduce further non-dimensional quantities: $\mathbf{x} = \boldsymbol{\xi}/L$ is the (non-dimensional) macroscale spatial coordinate with lengthscale L ; $\mathbf{y} = \boldsymbol{\xi}/l$ is the non-dimensional microscale spatial coordinate with lengthscale $l = rL$, with $r \ll 1$. We also have the non-dimensional potential and concentrations, $\psi = F\phi/[RT]$, $n^{\pm} = c^{\pm}/\bar{c}$, where \bar{c} is a representative concentration. In addition, \mathcal{C} denotes the microscale unit cell of the non-dimensional model, with fluid Y^f and solid Y^s subdomains, while $\mathcal{C} = Y^s \cup Y^f$, and the solid–fluid interface is denoted by $I = \partial Y^s \cap \partial Y^f$. Implementing the approach of Bruna et al. [10] for a similar, though simpler, problem of upscaling the diffusion equation in heterogeneous media, we consider the multiple scales procedure, with \mathbf{x} and \mathbf{y} considered independent variables, while $\nabla_{\mathbf{x}} \rightarrow \nabla_{\mathbf{x}} + r^{-1} \nabla_{\mathbf{y}}$. Similarly, we describe the interface via a level set function, allowing an asymptotic expansion of the boundary and interface conditions in the small parameter r .

Proceeding with the non-dimensional system, we expand the concentrations and potential in r

$$n^{\pm} = n_0^{\pm} + r n_1^{\pm} + r^2 n_2^{\pm} + O(r^3), \quad \psi = \psi_0 + r \psi_1 + r^2 \psi_2 + O(r^3),$$

for $r \ll 1$, with the aim of identifying the leading order behaviour in the macroscale spatial coordinate \mathbf{x} . As is standard in multiple scales, we require strict periodicity of n_j^{\pm} , ψ_j in the microscale variable \mathbf{y} for each cell domain \mathcal{C} [2,10,11]. In addition, only the leading order normal survives the leading order expansion and thus the geometry is that of the leading order problem only.

Noting that the temporal equilibration of ionic concentrations is fast [12], so that any transients due to any heterogeneity in the initial conditions relax on a timescale that is too fast to be of interest, the leading zeroth order solutions for n_0^{\pm} , ψ_0 are independent of \mathbf{y} . However, the next (first) order is key, as it affects the final upscaled equations and typically requires assumptions to enable an Ansatz that generates a cell level problem in auxiliary variables, which can subsequently be used to determine the macroscale model. We base our arguments at this stage only on the linearity of the governing first order equations and insights from nonequilibrium thermodynamics. The resulting cell problem, as determined in section 1.3 of the SM (Supplementary Material), reads

$$\partial_{y_i}(\varepsilon(\mathbf{x}, \mathbf{y}) \partial_{y_i} \Gamma_p) = -\partial_{y_p} \varepsilon(\mathbf{x}, \mathbf{y}), \quad \llbracket \varepsilon(\mathbf{x}, \mathbf{y}) \boldsymbol{\nu}_0 \cdot \nabla_{\mathbf{y}} \Gamma_p \rrbracket = -\llbracket \varepsilon(\mathbf{x}, \mathbf{y}) \nu_{0p} \rrbracket = -\llbracket \varepsilon(\mathbf{x}, \mathbf{y}) \rrbracket \nu_{0p},$$

and

$$\nabla_{\mathbf{y}}^2 \zeta_p^{\pm} = 0, \quad \boldsymbol{\nu}_0 \cdot \nabla_{\mathbf{y}} \zeta_p^{\pm} = -\nu_{0p},$$

for auxiliary functions Γ_p and ζ_p^{\pm} for $p \in \{1, 2, 3\}$ where we introduced the nondimensional permittivity $\varepsilon(\mathbf{x}) = \lambda^2(\mathbf{x})/L^2$ as the square of the ratio of the Debye length, $\lambda = \sqrt{\frac{\epsilon RT}{\bar{c} F^2}}$, and the macroscale lengthscale, L , and distinct from the electric permittivity, ϵ .

In turn, with

$$\rho_Q := \frac{1}{l|I|} \frac{1}{F\bar{c}} \int_I Q \, dS,$$

considering the solvability condition of the second order problem, via the Fredholm alternative, together with the transport theorem yields the upscaled macroscale equations (see SM 1.3 for full details)

$$\partial_{x_i} \left[M_{ip}^{\varepsilon, \Gamma}(\mathbf{x}) \partial_{x_p} \psi_0(\mathbf{x}) \right] = -\varphi(\mathbf{x}) (z^+ n_0^+(\mathbf{x}) + z^- n_0^-(\mathbf{x})) - \frac{|I|}{|C|} \rho_Q, \quad (4)$$

$$\varphi(\mathbf{x})\partial_\tau n_0^\pm(\mathbf{x}) = \nabla_{x_q} (L_{qp}^\zeta(\mathbf{x}) [\partial_{x_p} n_0^\pm(\mathbf{x}) + z^\pm n_0^\pm(\mathbf{x})\partial_{x_p} \psi_0(\mathbf{x})]), \quad (5)$$

where we denote the (nondimensional microscale) area of the interface $|I| = \int_I dS_y$ and the (nondimensional microscale) cell volume $|\mathcal{C}| = \int_{\mathcal{C}} dV_y$. Note that the integrals in the above are on the microscale y , with

$$M_{ip}^{\varepsilon, \Gamma}(\mathbf{x}) = \frac{1}{|\mathcal{C}|} \int_{\mathcal{C}} dV_y \varepsilon(\mathbf{x}, \mathbf{y}) [\partial_{y_i} \Gamma_p(\mathbf{x}, \mathbf{y}) + \delta_{ip}], \quad L_{ip}^\zeta(\mathbf{x}) = \frac{1}{|\mathcal{C}|} \int_{Y_f} dV_y [\partial_{y_i} \zeta_p(\mathbf{x}, \mathbf{y}) + \delta_{ip}]. \quad (6)$$

Finally, as derived in detail in Section 1.3 of SM, the leading order swelling pressure is given via

$$-\nabla_x p_0^{sw}(\mathbf{x}) = RT\bar{c}(z^+ n_0^+ + z^- n_0^-) \nabla_x \psi_0(\mathbf{x}). \quad (7)$$

3. Illustration — the swelling pressure in a heterogeneous system

We now consider the derived leading order upscaled PNP equations with a weakly heterogeneous system, dropping the index 0 for convenience. The setting is suitable for exploring the limits of Donnan membrane theory, which is widely applied beyond its natural setting of two dilute electrolyte media separated by a membrane to phenomenologically represent swelling pressure in cartilage models [13,14].

Consider the following osmotic experiment with a static compressed cartilage sample; thus, the dynamics of its ions is considered in the context of a charged porous medium. Furthermore, we consider a typical experimental geometry, with a cuboidal block of cartilage, approximately 1 mm in height, tightly fitted into a solid impermeable cavity, with the top of the specimen compressed via a porous plunger, so that the top of the cartilage can be maintained in equilibrium with an ion bath [15]. Assuming only variation in the depth of the sample, the problem is effectively one-dimensional [12,15]. Note that for symmetric cell problems we have that L_{ij} , $M_{ij} \propto \delta_{ij}$ and hence with $L_{ij} = L^\zeta \delta_{ij}$, $M_{ij} = M^{\varepsilon, \Gamma} \delta_{ij}$ the two scalars L^ζ , $M^{\varepsilon, \Gamma}$ are sufficient to assess the transport and electric conductance properties of the material. Finally, we consider the permittivity of the solid phase to be zero while the permittivity of the electrolyte is constant.

Therefore, with x being the spatial coordinate that increases with sample depth, the governing equations for ion concentrations are

$$0 = (L^\zeta(x)(n^\pm)' + z^\pm n^\pm \psi')', \quad - (M^{\varepsilon, \Gamma}(x)\psi')' = \varphi(z^+ n^+ + z^- n^-) + \rho_Q \frac{|I|}{|\mathcal{C}|}, \quad (8)$$

with the prime $'$ denoting the spatial macroscale derivative d/dx . These bulk equations are accompanied by zero flux of ions at the bottom of the cartilage, at $x = 0$, while the bath at the top of the tissue, at $x = h$, contains a salt, NaCl, which dissociates into two ionic species c^\pm , so that we set the concentration scale to be the bath concentration $\bar{c} = c_B = c^+ = c^-$, with electroneutrality and thus no electric potential in the bath. Hence, we have the conditions

$$(n^\pm)'(x = 0) = 0, \quad n^\pm(x = h) = 1, \quad \psi'(x = 0) = 0, \quad \psi(x = h) = 0. \quad (9)$$

where setting $\psi(x = h) = 0$ fixes the gauge freedom in ψ . To simplify the discussion by allowing analytical progress and to focus on a single effect, we only consider a homogeneous volume fraction φ and retain spatial heterogeneity only in $Q(x)$, noting that fixed charge density is known to vary with depth in cartilage tissue and is considered important for tissue response [12,15].

One of the advantages of the presented upscaling approach is the direct link between macroscale parameters and microscale physics and domain geometry. We chose the cylindrical approximation of glycoaminoglycan chains organised in parallel for simplicity (see the SM for spherical solid insertions which provide an upper estimate for the influence of fixed charge due to the highest surface-to-volume ratio). We may employ Rayleigh's approximation for discs yielding [16]

$$L^\zeta(\varphi) = 1 - \frac{2(1 - \varphi)}{1 + (1 - \varphi) - 0.3058(1 - \varphi)^4}, \quad (10)$$

which approximates L^ζ up to $1 - \varphi < 0.7$ [10]. Note that we can explicitly see the effect of the volume fraction φ and, in our setting, the second macroscale coefficient is given by $M^{\varepsilon, \Gamma} = \varepsilon L^\zeta$ (recall that the nondimensional permittivity ε is constant in each phase and nonzero only in V^f).

First, note the following geometrical relations between the microscale lengthscale l , the radius of the solid cylinder a , and volume fraction φ :

$$l = a \sqrt{\frac{\pi}{1 - \varphi}}, \quad \frac{|I|}{|C|} = \frac{1}{\int_C dV_y} \int_I dS_y = 2\sqrt{\pi(1 - \varphi)}. \quad (11)$$

Next, we estimate the values of the physical parameters in the upscaled model from [14], where they compared the Donnan membrane theory to the microscale PNP equations and hence measured and estimated similar parameters:

$$c_B = 0.15 \text{ M}, \quad T = 293 \text{ K}, \quad \epsilon = 6.93 \times 10^{-10} \text{ F/m}, \quad z^\pm = \pm 1 \quad (12)$$

yielding a Debye length of $\lambda = 1.1 \text{ nm}$. Therefore, $\varepsilon = \lambda^2/L^2 = 1.21 \times 10^{-12}$, and we estimate the average value of the fixed charge density to be $Q = 0.0723 \text{ C/m}^2$, with $\rho_Q = Q/(lF\bar{c}) \approx 2.43$ [14]. Finally, for the average fluid volume fraction, we consider $\varphi = 0.775$ [15].

The first equation of ((8)a) can be readily solved to give

$$n^\pm(x) = \exp\left(-z^\pm \frac{\psi(x)}{L^\zeta}\right),$$

which is the usual Maxwell distribution of ion concentration. In turn, the electric potential satisfies

$$-\varepsilon L^\zeta \psi'' = 2\varphi \sinh(-\psi/L^\zeta) + 2\rho_Q(x) \sqrt{\pi(1 - \varphi)}, \quad (13)$$

where $\varepsilon \approx 10^{-12}$ and $L^\zeta \approx 0.63$, supplemented by the potential boundary conditions of Eqn (9). Hence, one can observe that the potential ψ , and hence the osmotic pressure p^{sw} , possess two distinct parts: (i) a boundary layer solution that allows the boundary conditions of (9) to be satisfied and (ii) the bulk solution that emerges from the dominant balance between the fixed charge density ρ_Q and the ions, as represented by the sinh term.

To better understand the structure of each contribution, we quasi-linearise the differential equation into (see SM 1.3 for its plausibility and precision of this approximation)

$$\varepsilon \psi'' = \frac{2\varphi}{(L^\zeta)^2} \left(\psi - L^\zeta \operatorname{arcsinh}\left(\frac{1}{\varphi} \rho_Q(x) \sqrt{\pi(1 - \varphi)}\right) \right)$$

and perform a boundary layer analysis via a direct solution computation and Laplace's method rather than considering WKBJ, as detailed in SM 1.3. This generates an approximate solution with a boundary layer of rapid growth of the electrical potential at, and only at, $x = h$ on a lengthscale $\sqrt{\varepsilon L^\zeta/(2\varphi)}$, as given by

$$\psi(x) \approx L^\zeta \operatorname{arcsinh}\left(\frac{1}{\varphi} \rho_Q(x) \sqrt{\pi(1 - \varphi)}\right) \left(1 - e^{-\frac{1}{L^\zeta} \sqrt{\frac{2\varphi}{\varepsilon}}(h-x)}\right). \quad (14)$$

In particular, away from the boundary layer, the potential satisfies

$$\psi(x) \approx L^\zeta \operatorname{arcsinh}\left(\frac{1}{\varphi} \rho_Q(x) \sqrt{\pi(1 - \varphi)}\right),$$

on the self-consistent neglect of exponentially small errors. Finally, we may estimate the magnitude of both contributions in the above-mentioned typical situation in cartilage. From the above relations we have

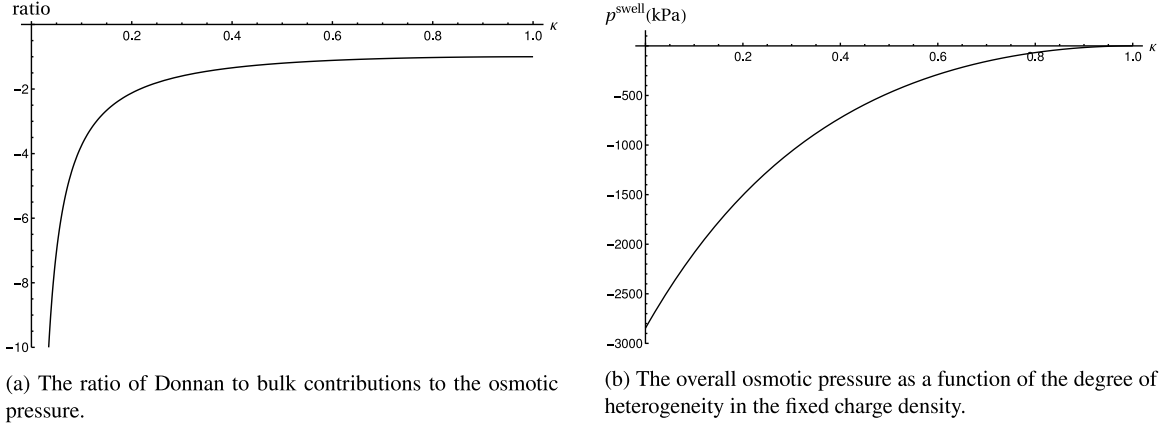


Fig. 1. An assessment of the significance of the novel bulk contribution to the osmotic pressure using the following measure of heterogeneity $\rho_Q(0) = (1 - \kappa)\rho_Q(h)$. In Figure (a) we plot the ratio $p_{Donnan}^{sw}/p_{bulk}^{sw}$, while in Figure (b) we plot $p^{sw} = p_{Donnan}^{sw} + p_{bulk}^{sw}$ according to Eq. (16).

$$\begin{aligned}
 p^{sw}(x) &= -RT\bar{c} \int_x^h (n^+ - n^-) \psi'(z) dz = -RT\bar{c} \int_x^h 2 \sinh(-\psi/L^\zeta) \psi'(z) dz \\
 &= -2RT\bar{c}L^\zeta \left(\cosh\left(\frac{\psi(x)}{L^\zeta}\right) - \cosh\left(\frac{\psi(h)}{L^\zeta}\right) \right). \quad (15)
 \end{aligned}$$

With $\chi := \sqrt{\pi(1 - \varphi)}/\varphi$ and using the approximation of Eqn (14), the swelling pressure across the entire cartilage specimen is given by

$$p^{sw}(0) = -2RT\bar{c}L^\zeta \left[\underbrace{\left((\chi^2 \rho_Q^2(h) + 1)^{1/2} - 1 \right)}_{\text{Donnan, } p_{Donnan}^{sw}} + \underbrace{\left((\chi^2 \rho_Q^2(0) + 1)^{1/2} - (\chi^2 \rho_Q^2(h) + 1)^{1/2} \right)}_{\text{bulk, } p_{bulk}^{sw}} \right], \quad (16)$$

which has been decomposed into a boundary layer Donnan term and a bulk term. In particular, the former has the same functional form as Donnan membrane theory predictions for swelling pressure [14], except for volume fraction corrections from the parameters L^ζ and χ , together with a bulk correction that is zero in the case of homogeneous fixed charge.

Noting that the bulk contribution is nonzero only if there is spatial heterogeneity in the fixed charge, and the highest concentration could be expected at the location of the porous plunger compression at the top of the cartilage, $x = h$ [15]), we denote a measure of such variation via κ , with $\rho_Q(0) = (1 - \kappa)\rho_Q(h)$. With the above estimate of fixed charge density of $\rho_Q(h) = 2.43$, we plot how heterogeneity, characterised via κ , impacts the ratio of the two contributions to the swelling pressure in Fig. 1(a), with the corresponding swelling pressure in Fig. 1(b). For example, one can observe that with a heterogeneity on the order of 10% across the sample, the novel bulk contribution, p_{bulk}^{sw} constitutes a third of the overall swelling pressure. In addition, as the osmotic pressure in such a situation is measured to be approximately 200 kPa [14], we have $\kappa \approx 0.66$ and the two contributions are of the same order, namely $p_{Donnan}^{sw}/p_{bulk}^{sw} = -1.076$. Therefore, the bulk contribution actually counterbalances the osmotic pressure at the boundary layer interface and, more generally, substantial heterogeneity in the osmotic pressure with depth when there is, for example, a linear change of 10% in the fixed charge across the depth of the sample.

4. Discussion

Using the framework of Bruna et al. [10] we have obtained an upscaled version of the Poisson-Nernst-Planck equation with periodicity except, in general, for a long lengthscale heterogeneity. In the derivation, there is an expansion in both $r = l/L$ and $\varepsilon = \lambda/L$, so that both are assumed to be small. Physiologically, for cartilage, one might expect $0 < \varepsilon < r$, as the Debye layer will be of a lengthscale smaller than that repeating cell, \mathcal{C} , and possibly much smaller, though such scalings are consistent with the approximations used in the derivation of the macroscale model. Further, the fact $r \ll 1$ and $\varepsilon \ll 1$ for typical cartilage parameters indicates that even though only a leading order macroscale model is derived, the level of approximation should be excellent.

In addition, the upscaled model has retained an analogous structure to the microscale formulation, with the same definition of the thermodynamic force via the electro-chemical potential, except that the phenomenological coefficient is, in general, a tensor and contains fine-scale geometrical detail of the microscale interactions. A recent article by Bazant and Schmuck considered the upscaling of a similar model, especially once fluid flow is neglected, though spatial heterogeneity on the macroscale was not considered [2]. The macroscale model emerging from upscaling reveals a different structure, where ion transport is driven by two independent driving forces for each ion species [2]. This outcome can be traced to a thermodynamically motivated assumption that was introduced in order to separate out the cell problem, as briefly summarised in SM Section 2. The approach proposed here in contrast presents advantages such as (i) the physically motivated Ansatz, following from the linear nature of the governing equations (see SM Section 2 for more details), (ii) the equilibrium concentration of ions follow the expected Boltzmann distribution, (iii) the recognised macroscale thermodynamic force for transport is the classical electrochemical potential, (iv) the Einstein mobility–diffusion relation and the related fluctuation–dissipation theorem suggesting that the macroscale thermodynamic forces should match those on the microscale, as also implicit in the Onsager relations and widely considered to be valid in particular in transport phenomena [17,18]. In this sense, we consider the macroscale model to be thermodynamically consistent with microscale thermodynamics.

On completing the upscaling of the PNP equations, with the quasi-linear approximation, the resulting leading order macroscale model first reveals a boundary layer contribution, with a clear link to the phenomenological use of Donnan membrane theory in the literature for cartilage modelling [13]. In turn, this reveals why the phenomenological use of Donnan membrane theory nonetheless generates good predictions for cartilage swelling pressure, at least in perfectly periodic settings with no further heterogeneity. However, with fixed charge heterogeneity in the bulk, a further contribution to the swelling pressure is predicted. In particular, this is significant even in standard applications given a relative change of 10% in fixed charge across the sample depth, highlighting the predicted sensitivity of swelling pressure to heterogeneity in cartilage fixed charge. We further note that the boundary layer and bulk structure of the behaviour of the predicted swelling pressure in the macroscale model presented here differ from other modelling studies. Although most studies modelling cartilage do not attempt to rationally upscale in the presence of heterogeneity, an exception is a macroscale model based on a multiple scales approach (Whiteley et al. [7]), which does not have an analogue of the bulk term induced by heterogeneous fixed charge. Hence, while there is still further work in understanding the similarities and differences in the emergent models from different upscaling procedures [5], this is exacerbated further in the presence of heterogeneity, for exploration in future work.

CRediT authorship contribution statement

Václav Klika: Conceptualisation, Methods, Write up. **Eamonn A. Gaffney:** Methods, write up.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.aml.2022.108482>.

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