Weierstraß-Institut für Angewandte Analysis und Stochastik

Leibniz-Institut im Forschungsverbund Berlin e. V.

Preprint

ISSN 2198-5855

A kinetic model of a polyelectrolyte gel undergoing phase separation

Giulia L. Celora¹, Matthew G. Hennessy¹, Andreas Münch¹, Barbara Wagner²,

Sarah L. Waters¹

submitted: December 22, 2020

2

¹ Mathematical Institute Andrew Wiles Building, Woodstock Road Oxford, OX2 6GG UK E-Mail: celora@maths.ox.ac.uk hennessy@maths.ox.ac.uk muench@maths.ox.ac.uk waters@maths.ox.ac.uk Weierstrass Institute Mohrenstr. 39 10117 Berlin Germany E-Mail: barbara.wagner@wias-berlin.de

No. 2802 Berlin 2020



2010 Mathematics Subject Classification. 74A30, 80A22, 34B15.

2010 Physics and Astronomy Classification Scheme. 83.80.Rs, 83.10.Tv.

Key words and phrases. Polyelectrolyte gel, phase separation, non-equilibrium thermodynamics.

MH recognizes support from the Mathematical Institute through a Hooke fellowship, and GC acknowledges support through a Dphil scholarship from the SABS CDT, University of Oxford.

Edited by Weierstraß-Institut für Angewandte Analysis und Stochastik (WIAS) Leibniz-Institut im Forschungsverbund Berlin e. V. Mohrenstraße 39 10117 Berlin Germany

Fax:+493020372-303E-Mail:preprint@wias-berlin.deWorld Wide Web:http://www.wias-berlin.de/

A kinetic model of a polyelectrolyte gel undergoing phase separation

Giulia L. Celora, Matthew G. Hennessy, Andreas Münch, Barbara Wagner, Sarah L. Waters

Abstract

In this study we use non-equilibrium thermodynamics to systematically derive a phase-field model of a polyelectrolyte gel coupled to a thermodynamically consistent model for the salt solution surrounding the gel. The governing equations for the gel account for the free energy of the internal interfaces which form upon phase separation, as well as finite elasticity and multicomponent transport. The fully time-dependent model describes the evolution of small changes in the mobile ion concentrations and follows their impact on the large-scale solvent flux and the emergence of long-time pattern formation in the gel. We observe a strong acceleration of the evolution of the free surface when the volume phase transition sets in, as well as the triggering of spinodal decomposition that leads to strong inhomogeneities in the lateral stresses, potentially leading to experimentally visible patterns.

1 Introduction

A polyelectrolyte gel is a network of covalently cross-linked polyelectrolyte macromolecules that carry fixed charges and/or ionizable groups and are immersed in a solvent. If placed in a salt solution, hereafter referred to as an *ionic bath*, polyelectrolyte gels can undergo chemical, electrical, and mechanical interactions with the surrounding ionic bath, all of which can trigger structure formation in the gel. To capture these interactions, we derive a thermodynamically consistent model for the polyelectrolyte gel and the surrounding ionic bath. The governing equations in the gel and ionic bath are coupled together via appropriate interfacial conditions.

Exchange of solvent and mobile ions between the ionic bath and the polyelectrolyte gel will drive the system towards a new equilibrium. The transition to the new equilibrium typically involves a volume phase transition in the form of swelling or collapse of the gel [47, 77], and has been widely discussed both experimentally and theoretically [2, 10, 11, 18, 32, 49, 51, 67]. This process depends in a subtle way on the concentration and valency of the salt in the solvent, the material properties of the macro-molecules including the degree of fixed charge, and externally applied fields, such as temperature or an electric field. When considering the transient evolution of the gel between the different equilibria, phase separation can occur whereby regions of highly swollen and collapsed gel can co-exist in the material. As shown experimentally by Tanaka et al. [47, 68], this can give rise to surface instabilities which can transiently or permanently affect the gel morphology and its resulting properties. Moreover, small changes in the salt concentration in the surrounding ionic bath can have dramatic effects on the gel state and can result in discontinuous phase transitions connected with super-collapse [34, 39] or re-entrant swelling [63]. Changes in the surrounding environment of the gel can also result in micro- or nanophase separation [62, 69], or arrested phase separation and reverse Ostwald ripening [58, 59], and these features play an important role in subcellular organelle formation [5, 66].

While aspects of gel dynamics can be explored in the context of neutral hydrogels [17, 28, 31], models for polyelectrolyte gels immersed in an ionic bath enable pattern formation phenomena that arise due to local environmental parameters to be explored. Such phenomena have important biological functions and medical applications [29, 42, 43]. In regenerative medicine, for example, polyelectrolyte gels can be used as scaffolds for biological cells, and the resulting cell-seeded gels can be cultured to engineer replacement biological tissues [43, 46, 52]. The local electromechanical environment experienced by cells within these polyelectrolyte scaffolds can be controlled by the application of, for example, an external electric field, so that these bio-active materials can be utilised to guide and direct cell behaviour. Polyelectrolyte gels are also used as model systems for fundamental biological phenomena, including biological tissues such as cartilage and brain [20, 46], or as a model for bio-macromolecules such as DNA, RNA [21, 57, 75]. Phase separation of environmentally sensitive polyelectrolyte gels is also fundamental to the development of smart, responsive materials and sensors [6, 8, 29, 65].

To capture the underlying physics, which combines aspects of electrochemistry and condensed matter physics, we use non-equilibrium thermodynamics and systematically derive a phase-field model of a polyelectrolyte gel that accounts for the free energy of the internal interfaces which form upon phase separation, as well as for finite elasticity. We also derive a thermodynamically consistent model for the ionic bath. In contrast to the polyelectrolyte gel, the ionic bath does not have a well-defined reference configuration, which leads to subtle differences when using our thermodynamic framework to obtain constitutive relationships. The governing equations for the bath that we derive are similar to those obtained for liquid electrolytes [14, 60] used in electrochemical storage systems such as batteries. Our model accounts for multi-component transport (solvent and mobile ions) between the ionic bath and gel. To account for the dissipation due to the relative motion of the solvent and ions we use a Stefan-Maxwell approach to account for cross-diffusion. It is well-known that multi-component transport may lead to anomalous diffusivities if the underlying theory assumes that diffusion of a species is solely driven by the gradient of its chemical potential [41]. The Stefan-Maxwell approach [48, 64] correctly captures the hydrodynamic drag between different components of the mixture by balancing the friction forces between the different species [3]. While having been previously ignored for polyelectrolyte gels [31], the recent work by Zhang et al. [76] has highlighted the role of cross-diffusion in modelling effects such as a temporary excess of salt entering the hydrogel during swelling, which is subsequently rejected as the gel approaches its new equilibrium.

The governing equations for the polyelectrolyte gel and ionic bath must be coupled via the specification of appropriate interfacial conditions for the double-layer that is established between the bath and the gel. While Mori et al. [50] derived a coupled model for a polyelectrolyte gel in contact with a solvent bath, they did not consider phase separation in the gel nor Stefan–Maxwell diffusion. In a companion paper [27], we use matched asymptotic expansions to derive the corresponding electroneutral model for the gel-bath system with consistent jump conditions to be imposed across the thin electric double layer which forms at the gel-bath interface.

The model presented in this paper can thus capture the fully time-dependent hydrodynamics of the ionic bath, and the mechanical interactions between the gel and the ionic bath. The model can be exploited to determine how the fast dynamics of ion migration affects the much slower transport of the solvent, which in turn provides mechanistic insights into the transient dynamics of the emerging patterns within the gel en route to a new equilibrium state. This theoretical framework enables new interpretations of experimental results as it can be used as a tool to discover and investigate the phenomena of phase separation in polyelectrolyte gels.

In §2, we derive the model for the polyelectrolyte gel by formulating the conservation laws, constructing the free energies, and using the approach by Gurtin [25, 26] to derive the constitutive equations via an

energy imbalance inequality. The full model for the ionic bath is derived in §3 using a similar approach. The interfacial conditions between the gel and ionic solutions are given in §4.

Some first insights into the potential of the model to predict the emergence of patterns in the gel as a function salt concentration, the Flory-Huggins parameter χ and/or elastic modulus of the network of polyelectrolyte macromolecules, are discussed in §5, where we explore numerically the dynamics of swelling and collapse of a constrained gel. We use our model to resolve the transient dynamics of the volume phase transition. Specifically, we show how the initial dynamics, governed by the flux of the mobile ions, determines the long-time front propagation from the free interface that eventually leads to the volume phase transition. In some cases, this transition is also accompanied by the emergence of local collapsed states that arise due to spinodal decomposition ahead of the main transition front. Interestingly, in the collapsed regions, the ion concentration is higher and corresponds to higher tensile stresses, suggesting the emergence of patterns that may be observed in experiments. The numerical results presented here are extended in a companion paper [7], where we also carry out a linear stability analysis to capture the spinodal decomposition together with a phase-plane analysis to show the existence of the transition fronts.

2 Model derivation for a polyelectrolyte gel

In this section we derive the governing equations describing the behaviour of a polyelectrolyte gel. In §2.1 we describe the components of the polyelectrolyte gel, and introduce the reference (dry) and current (swollen) configurations. In §2.2 we present the equations representing incompressibility of the polyelectrolyte gel, conservation of mass of the mobile species, and conservation of momentum of the gel. These are complemented with the definition of the electrostatic potential and Gauss' law of electrostatics for the electric displacement. The equations are presented in both the reference and the current configurations. In §2.3 we construct the free energy of the system. We then apply the energy imbalance inequality of Gurtin [26] to obtain thermodynamically consistent expressions for the state equations (constitutive relationships) in terms of the previously specified free energy (§2.4). In §2.5 we consider the rate of entropy production to determine relationships for the mass fluxes. Finally in §2.6 present the full model equations (conservation laws together with state equations) in the current state.

2.1 Kinematics

We consider the gel as a multi-phase material composed of a solid polymer network with fixed charges and a solution consisting of solvent, such as water, and N freely moving ionic species (*i.e.* solutes), see Figure 1. We assume all phases are intrinsically incompressible and isotropic. We note that the solid phase volume encompasses the fixed charge volume. Throughout the model derivation, we use subscripts n, s to denote the solid polymer network and solvent respectively, index $i = 1, \ldots, N$ to denote the ionic species, and the index $m \in \{s, 1, \ldots, N\}$ to refer to the species that are mobile relative to the network, *i.e.* both the solvent and solutes. For later convenience, we introduce the set notation $\mathbb{I} = \{1, \ldots, N\}$ and $\mathbb{M} = \{s, 1, \ldots, N\}$.

The motivation for this study is to understand the swelling behaviour of a polyelectrolyte gel in contact with an ionic solution. By changing the solution conditions, such as the concentration of ions, the polyelectrolyte gel will swell. To capture this, we consider the gel in an initially pre-swollen state in contact with an ionic solution, and then change the solution conditions. As shown in Figure 2, this configuration differs from the reference state which is stress free and is assumed to be the dry gel,



Figure 1: Schematic representation of a polyelectrolyte gel in contact with an ionic solution. The gel is a three-phase material, composed of solid polymer network with fixed changes, solvent, and freely moving ions. The polyelectrolyte gel is surrounded by an ionic solution consisting of solvent and freely moving ions.



Figure 2: Sketch of the reference, initial and current state of the gel.

i.e. only solid phase present. As the gel deforms, the material element located at X (Lagrangian coordinates) in the reference configuration \mathcal{B}_R is displaced to the point x (Eulerian coordinates) in the current configuration \mathcal{B} as shown in Figure 2. Such a transformation is described by the deformation gradient tensor $\mathbf{F} = \partial x / \partial X$; information about the change in volume during deformation is encoded

in $J = \det \mathbf{F}$, while $\boldsymbol{u} = \boldsymbol{x} - \boldsymbol{X}$ is the displacement vector. As the gel deformation is determined by the displacement of the solid phase, the solid phase velocity in the current configuration, \boldsymbol{v}_n , and displacement are related, so that $\boldsymbol{v}_n = \dot{\boldsymbol{u}}$ where dots denote derivatives with respect to time in the reference configuration, *i.e.* $\partial/\partial t|_{\boldsymbol{X}} \boldsymbol{u}$.

2.2 Conservation equations

As the solid phase is incompressible, any change in the volume during deformation is due to the migration of solvent and solute molecules, whose nominal ¹ concentrations are denoted by C_s and C_i respectively ($i \in \mathbb{I}$). This leads to the molecular incompressibility condition:

$$J = 1 + \sum_{m \in \mathbb{M}} \nu_m C_m, \tag{2.1a}$$

where ν_m ($m \in \mathbb{M}$) is the characteristic molecular volume of each species in the solution.

Mass conservation for each mobile species in the reference configuration reads:

$$C_m + \nabla_R \cdot \boldsymbol{J}_m = 0, \tag{2.1b}$$

where J_m is the nominal flux per unit area in the reference state and ∇_R denotes the gradient with respect to the Lagrangian coordinates X.

When considering gels, inertial and gravitational effects are commonly neglected, so that the conservation of momentum for the gel reads:

$$\nabla_R \cdot \mathbf{S} = \mathbf{0},\tag{2.1c}$$

where **S** is the first Piola-Kirchoff tensor, which represents the stress state of the polyelectrolyte gel in the reference configuration. The presence of free moving ions generates an electric field which is denoted by E in the reference configuration. Introducing the electrostatic potential Φ , we have that:

$$oldsymbol{E} = -
abla_R \Phi,$$
 (2.1d)

As in [29], we consider the gel to be a dielectric material². Consequently, the presence of the electric field generates an electric displacement H^3 , which must obey Gauss' law of electrostatics:

$$\nabla_R \cdot \boldsymbol{H} = Q = e\left(\sum_{i \in \mathbb{I}} z_i C_i + z_f C_f\right),$$
(2.1e)

where Q is the local total charge, which accounts for both fixed and moving charges, e is the elementary charge, C_f is the nominal concentration of fixed charges and z_i is the valence of the corresponding charged species.

Equations (2.1a), (2.1b), (2.1c), (2.1d) and (2.1e) are the incompressibility condition, conservation of mass and momentum, the definition of electric potential, and Gauss law of electrostatics, all written

¹variable value in the reference configuration

²a material that does not conduct electricity but can be polarized in the presence of an electric field.

³the vector field that accounts for both the electric field and the polarization of the dielectric material.

with respect to the reference configuration. Our goal is to derive a mathematical model for the polyelectrolyte in the current configuration, to facilitate quantitative comparison with experimental data. We move from governing equations in the reference state for the nominal quantities to the corresponding equations in the current configuration as follows. Given a volume element dV_R and its surface element NdS_R in the reference configuration, these are related to the analogous quantities dV and ndS in the current configuration by the relations:

$$dV = JdV_R,$$
(2.2a)

$$\boldsymbol{n}dS = J \boldsymbol{\mathsf{F}}^{-T} \boldsymbol{N} dS_R, \tag{2.2b}$$

where N and n are respectively the normal unit vector to the surface elements dS_R and dS respectively, see Figure 2.

We define the concentration of mobile species in the current state to be $c_m = C_m/J$. The incompressibility condition (2.1a) in the current state then reads

$$J = \frac{1}{1 - \sum_{m \in \mathbb{M}} \nu_m c_m}.$$
(2.2c)

The conservation of mass equations in the current state are given by (see Appendix A)

$$\partial_t c_m + \nabla \cdot (c_m \boldsymbol{v}_n) = -\nabla \cdot \boldsymbol{j}_m,$$
 (2.2d)

where ∇ denotes the gradient, $v_n = \partial u / \partial t + (v_n \cdot \nabla) u$ is the network velocity, and j_m is the flux for the *m*-th species which is related to J_m by the following identity:

$$\boldsymbol{J}_m = J \boldsymbol{\mathsf{F}}^{-1} \boldsymbol{j}_m. \tag{2.2e}$$

We define the velocity of the mobile species to be v_m , and relate it to the flux j_m as follows:

$$\boldsymbol{j}_m = c_m \left(\boldsymbol{v}_m - \boldsymbol{v}_n \right) = c_m \bar{\boldsymbol{v}}_m,$$
 (2.2f)

where, for later convenience, we introduce the notation \bar{v}_m for the relative velocity of the *m*-th phase with respect to the network velocity.

When considering conservation of momentum (2.1c), the counterpart to the first Piola-Kirchoff tensor **S** in the current configuration is the Cauchy stress tensor **T**, which is related to **S** as follows:

$$\mathbf{T} = J^{-1} \mathbf{S} \mathbf{F}^T. \tag{2.2g}$$

Conservation of momentum in the current state is

$$\nabla \cdot \mathbf{T} = \mathbf{0}. \tag{2.2h}$$

Finally, by applying the following rules:

$$\boldsymbol{H} = J \boldsymbol{\mathsf{F}}^{-1} \mathbf{h}, \tag{2.2i}$$

$$\boldsymbol{E} = \boldsymbol{\mathsf{F}}^T \mathbf{e},\tag{2.2j}$$

where h and e are respectively the electric displacement and field in the current configuration, equations (2.1d)-(2.1e) are now:

$$e = -\nabla \Phi,$$
 (2.2k)

$$\nabla \cdot \boldsymbol{h} = \frac{Q}{J} = e\left(\sum_{i \in \mathbb{I}} z_i c_i + z_f c_f\right).$$
(2.2)

In summary, the corresponding incompressibility condition, conservation of mass and momentum, electrostatic potential definition and Gauss' law of electrostatics in the current configuration are equations (2.2c), (2.2d), (2.2h), (2.2k) and (2.2l), where the network velocity is $v_n = \partial u / \partial t + (v_n \cdot \nabla) u$. In §2.4, we determine how the constitutive relationships relate to the (as yet unspecified) free energy of the system via the use of the energy imbalance inequality of Gurtin [25].

2.3 Free energy

Equations of state that are consistent with the second law of thermodynamics can be derived by specifying the precise form of the free energy per unit volume in the reference configuration Ψ . We assume that the free energy is composed of five contributions as follows

$$\Psi = \Psi_1 + \Psi_2 + \Psi_3 + \Psi_4 + \Psi_5, \tag{2.3}$$

corresponding to the energy of the electric field (Ψ_1) ; the energy of the solvent and solutes not interacting with each other or the solid phase (Ψ_2) ; the mixing energy of the difference phases (Ψ_3) ; the interfacial energy between dissimilar phases (Ψ_4) ; and the energy of the solid phase not interacting with the solution (Ψ_5) , *i.e.* the elastic energy of the gel.

Assuming the polyelectrolyte gel to be an ideal and linear dielectric material, with constant permittivity ϵ , the free energy of polarization is given by [15, 29]:

$$\Psi_1 = \frac{1}{2\epsilon J} \boldsymbol{H} \boldsymbol{F}^T \cdot \boldsymbol{F} \boldsymbol{H}.$$
(2.4)

We assume that the permittivity is dominated by the permittivity of the solvent, with little contribution from the network or mobile phases.

The second energy density Ψ_2 has the standard form [17]:

$$\Psi_2 = \sum_{m \in \mathbb{M}} \mu_m^0 C_m \tag{2.5}$$

where μ_m^0 denotes the chemical potential of non interacting solvent and ion molecules.

When considering the mixing energy, a common assumption in the study of polyelectrolyte gels is that the leading contribution to the enthalpy arises from the solvent due to the hydrophobic interaction with the solid phase[35]. According to Flory-Huggins theory [22, 36] of mixtures, the mixing energy Ψ_3 is then given by:

$$\Psi_3 = k_B T \left(\frac{\chi C_s}{1 + \sum_{j \in \mathbb{M}} \nu_j C_j} + \sum_{m \in \mathbb{M}} C_m \ln \frac{\nu_m C_m}{1 + \sum_{j \in \mathbb{M}} \nu_j C_j} \right),$$
(2.6)

where k_B is the Boltzmann's constant, T is the temperature and χ is the Flory interaction parameter (capturing the enthalpy of mixing the solvent and solid phase).

The effect of interfacial tension may be included by considering interfacial energy contributions. For multiple phases, and assuming ideal interfaces [30], candidate interfacial energy contributions expressed in the current configurations include [23]

$$\psi_{4} = \sum_{m \in n, \mathbb{M}} A_{m} |\nabla c_{m}|^{2} \text{ or } \psi_{4} = \sum_{\substack{l, m \in n, \mathbb{M} \\ l < m}} B_{lm} |c_{l} \nabla c_{m} - c_{m} \nabla c_{l}|^{2},$$
(2.7)

where the A_m and B_{lm} are constants, where here we use ψ to denote the free energy per unit volume of the *current configuration*. While our model formulation can accommodate contributions to the interfacial energy arising from gradients in all concentrations, here we consider the case for dilute ion concentrations, and assume that the interfacial energy contribution is dominated by gradients in the solvent concentration only. In the current configuration, we consider the specific form of ψ_4 to be

$$\psi_4 = \frac{\gamma}{2} \left| \nabla c_s \right|^2, \tag{2.8}$$

where γ plays a role analogous to surface tension (see also [55]). This interfacial energy expressed in the reference configuration is

$$\Psi_4 = \frac{\gamma}{2J} G_{iJ} G_{iM} \frac{\partial C_s}{\partial X_J} \frac{\partial C_s}{\partial X_M} + \frac{\gamma C_s^2}{2J^3} G_{iJ} G_{iM} \frac{\partial J}{\partial X_J} \frac{\partial J}{\partial X_M} - \frac{\gamma C_s}{J^2} G_{iJ} G_{iM} \frac{\partial C_s}{\partial X_J} \frac{\partial J}{\partial X_M}, \quad (2.9)$$

where $\mathbf{G} = \mathbf{F}^{-T}$.

Finally, for the strain energy we consider the gel to be a hyperelastic neo-Hookean material:

$$\Psi_5 = \frac{G}{2} \left(\mathbf{F} : \mathbf{F} - 3 - 2 \ln J \right)$$
(2.10)

where G is the shear modulus of the material.

Have specified the precise form of the free energy Ψ , we now go on to determine the constitutive relationships through consideration of the energy imbalance inequality of Gurtin [25, 26].

2.4 Energy imbalance inequality

As derived by Gurtin [25, 26] when considering an isothermal processes, the second law of thermodynamics can be rewritten in terms of the Helmholtz free energy Ψ leading to the *energy imbalance inequality*:

$$\frac{\mathsf{d}}{\mathsf{d}t} \left\{ \int_{\mathcal{V}_R} \Psi dV_R \right\} \le \mathcal{W}(\mathcal{V}_R) + \mathcal{M}(\mathcal{V}_R) \tag{2.11}$$

where \mathcal{V}_R is an arbitrary control volume of the system in the reference configuration \mathcal{B}_R , $\mathcal{W}(\mathcal{V}_R)$ is the rate at which the surrounding environment does work on \mathcal{V}_R and $\mathcal{M}(\mathcal{V}_R)$ is the rate of change of energy associated with the addition of mass due to transport processes.

The term $\mathcal{W}(\mathcal{V}_R)$ is decomposed into two contributions, the rate of electrical, $W_{el}(\mathcal{V}_R)$, and the rate of mechanical, $\mathcal{W}_{mec}(\mathcal{V}_R)$, work. Following [16], $\mathcal{W}_{el}(\mathcal{V}_R)$ is defined as:

$$\mathcal{W}_{el}(\mathcal{V}_R) = -\int_{\mathcal{S}_R} \Phi \, \dot{\boldsymbol{H}} \cdot \boldsymbol{N} dS_R, \qquad (2.12)$$

where S_R is the surface associated with the control volume V_R , and N is the unit normal vector to the surface S_R .

To determine the rate of mechanical work, $\mathcal{W}_{mec}(\mathcal{V}_R)$, we follow Gurtin [25] and account for the presence of both macro-stresses **S**, and micro-stresses $\boldsymbol{\xi}$, the latter of which arise due to the system heterogeneity[44]. We assume that the micro-stresses originate from gradients in the concentration of mobile species, *i.e.* solvent and ions. As the energy imbalance is formulated in the reference configuration \mathcal{B}_R , we replace c_m by C_m/J , with associated micro-stresses, denoted $\boldsymbol{\xi}_m$, $m \in \mathbb{M}$ and $\boldsymbol{\xi}_J$ respectively. The total rate of mechanical work $W_{mec}(\mathcal{V}_R)$ then reads:

$$\mathcal{W}_{mec}(\mathcal{V}_R) = \int_{\mathcal{S}_R} \mathbf{S} \mathbf{N} \cdot \dot{\mathbf{u}} \, dS_R + \sum_{m \in \mathbb{M}} \int_{\mathcal{S}_R} \left(\mathbf{\xi}_m \cdot \mathbf{N} \right) \dot{C}_m \, dS_R + \int_{\mathcal{S}_R} \left(\mathbf{\xi}_J \cdot \mathbf{N} \right) \dot{J} \, dS_R.$$
(2.13)

The system exchanges mass due to the diffusion of each mobile species, so $\mathcal{M}(\mathcal{V}_R)$ is given by:

$$\mathcal{M}(\mathcal{V}_R) = \sum_{m \in \mathbb{M}} - \int_{\mathcal{S}_R} \mu_m \, \boldsymbol{J}_m \cdot \boldsymbol{N} \, dS_R \,, \tag{2.14}$$

where μ_m is the chemical potential associated with each species.

Since equation (2.11) must hold for arbitrary control volumes \mathcal{V}_R^4 , substituting equations (2.12), (2.13) and (2.14) into the energy imbalance inequality (2.11), and applying the divergence theorem, we obtain the following localized inequality:

$$\dot{\Psi} + \sum_{i \in \mathbb{I}} \left[e \Phi z_i - \mu_i - \nabla_R \cdot \boldsymbol{\xi}_i \right] \dot{C}_i - \left(\mu_s + \nabla_R \cdot \boldsymbol{\xi}_s \right) \dot{C}_s - \left(\mathbf{S} + J \left(\nabla_R \cdot \boldsymbol{\xi}_J \right) \mathbf{F}^{-T} \right) : \dot{\mathbf{F}} - \mathbf{E} \cdot \dot{\mathbf{H}} - \boldsymbol{\xi}_J \cdot \nabla_R \dot{J} - \sum_{m \in \mathbb{M}} \boldsymbol{\xi}_m \cdot \nabla_R \dot{C}_m + \sum_{m \in \mathbb{M}} \nabla_R \mu_m \cdot \boldsymbol{J}_m \le 0,$$
(2.15)

where additionally we have exploited equations (2.1b) and (2.1c). We account for the constraint imposed by the incompressibility condition (2.1a) by differentiating with respect to time to give

$$\sum_{m \in \mathbb{M}} \nu_m \dot{C}_m - J \mathbf{F}^{-T} : \dot{\mathbf{F}} = 0,$$
(2.16)

and including the constraint (2.16) in (2.15) via a Lagrange multiplier p, where the multiplier p plays the role of the mechanical pressure.

Following [1, 25], guided by equation (2.15) we consider the free energy to have the following dependencies

$$\Psi = \Psi(\mathbf{F}, C_m, \nabla_R C_m, \nabla_R J, \mathbf{H}).$$
(2.17)

We highlight that we have retained the dependence of Ψ on $\nabla_R C_m$, $m \in \mathbb{M}$ to make explicit the relationship between the microstresses $\boldsymbol{\xi}_m$ and $\nabla_R C_m$ in the discussion that now follows. However, in the specification of the forms of the constitutive relationships in §2.3, the subsequent analysis will considerably simplify and we will retain only the microstresses $\boldsymbol{\xi}_s$ and $\boldsymbol{\xi}_J$. We also highlight that (2.17) precludes any explicit dependence of the free energy on the mass fluxes \boldsymbol{J}_m which are associated with an irreversible process, since, as species move relative to each other, friction is generated and energy is lost by the system.

Substituting (2.17) into (2.15), and including the constraint 2.16, we obtain the augmented form of the energy imbalance inequality:

$$\sum_{m \in \mathbb{M}} \left(\frac{\partial \Psi}{\partial \nabla_R C_m} - \boldsymbol{\xi}_m \right) \cdot \nabla_R \dot{C}_m + \left(\frac{\partial \Psi}{\partial C_s} - \mu_s - \nabla_R \cdot \boldsymbol{\xi}_s + p\nu_s \right) \dot{C}_s + \left(\frac{\partial \Psi}{\partial \boldsymbol{H}} - \boldsymbol{E} \right) \cdot \dot{\boldsymbol{H}} + \left(\frac{\partial \Psi}{\partial \nabla_R J} - \boldsymbol{\xi}_J \right) \cdot \nabla_R \dot{J} + \sum_{i \in \mathbb{I}} \left(\frac{\partial \Psi}{\partial C_i} + e\Phi z_i - \mu_i - \nabla_R \cdot \boldsymbol{\xi}_i + p\nu_i \right) \dot{C}_i$$

$$+ \left(\frac{\partial \Psi}{\partial \mathbf{F}} - \mathbf{S} - pJ\mathbf{F}^{-T} - J(\nabla_R \cdot \boldsymbol{\xi}_2)\mathbf{F}^{-T} \right) : \dot{\mathbf{F}} + \sum_{m \in \mathbb{M}} \nabla_R \mu_m \cdot \boldsymbol{J}_m \leq 0,$$
(2.18)

⁴We assume the control volume is not at the boundary between the polyelectrolyte gel and surrounding ionic solution.

Inequality (2.18) is linear in $\nabla_R \dot{C}_m$, \dot{C}_m , $\nabla_R \dot{J}$, \dot{H} , \dot{F} and $\nabla_R \mu_m$, each of which can be chosen independently at each point X and time t [25]. In particular, we can choose $\nabla_R \mu_m = 0$ and vary the other variables independently. The only way for the inequality (2.18) to be valid in all cases is to assume that the brackets are identically zero. This gives the following state equations

$$\boldsymbol{\xi}_{m} = \frac{\partial \Psi}{\partial \nabla_{R} C_{m}}, \quad m \in \mathbb{M},$$
(2.19a)

$$\boldsymbol{\xi}_J = \frac{\partial \Psi}{\partial \nabla_R J},\tag{2.19b}$$

$$\mu_s = \frac{\partial \Psi}{\partial C_s} - \nabla_R \cdot \boldsymbol{\xi}_s + p\nu_s, \qquad (2.19c)$$

$$\mu_{i} = \frac{\partial \Psi}{\partial C_{i}} - \nabla_{R} \cdot \boldsymbol{\xi}_{i} + e \Phi z_{i} + p \nu_{i}, \ i \in \mathbb{I}$$
(2.19d)

$$oldsymbol{E}=rac{\partial\Psi}{\partialoldsymbol{H}},$$
 (2.19e)

$$\mathbf{S} = \frac{\partial \Psi}{\partial \mathbf{F}} - pJ\mathbf{F}^{-T} + J(\nabla_R \cdot \boldsymbol{\xi}_2)\mathbf{F}^{-T}.$$
(2.19f)

The energy imbalance inequality (2.18) then reduces to:

$$\sum_{m \in \mathbb{M}} \nabla_R \, \mu_m \cdot \boldsymbol{J}_m \le 0. \tag{2.20}$$

Having identified the general form of the state equations for the dependent variables associated with the irreversible processes, in §2.5 we consider the irreversible process associated with mass transport and determine the equations relating the mass fluxes J_m and the chemical potential gradients $\nabla_R \mu_m$.

2.5 Derivation of transport laws

We consider dissipation only due to the diffusive transport of the mobile phases down gradients of chemical potential. As experimental measurements to determine drag coefficients correspond to quantities in the current configuration, we now revert to the current configuration. The analogy to the energy imbalance inequality (2.20) is the current configuration is [45]:

$$\sigma = -\sum_{m \in \mathbb{M}} c_m \nabla \, \mu_m \cdot \bar{\boldsymbol{v}}_m \ge 0, \tag{2.21}$$

where σ is the rate of entropy production per unit volume of the current configuration \mathcal{B} , and we have exploited the relationship between the fluxes j_m and the relative velocities of the mobile species \bar{v}_m given in equation (2.2f).

The theory of linear non-equilibrium thermodynamics states that, for systems sufficiently close to equilibrium, the dissipation rate σ is a quadratic function of the relative velocities [56]:

$$\sigma = \sum_{m \in \mathbb{M}} \sum_{\beta \in \mathbb{M}} \ell_{m\beta} \bar{\boldsymbol{v}}_{\beta} \cdot \bar{\boldsymbol{v}}_{m}, \qquad (2.22)$$

where $\ell_{m\beta}$ are *phenomenological coefficients*, chosen to satisfy the *Onsager reciprocal relations*[54], which in the absence of magnetic effects reads $\ell_{m\beta} = \ell_{\beta m}$ so that the matrix of phenomenological coefficients $\boldsymbol{\ell} = [\ell_{m\beta}]$ is positive semi-definite. Equations (2.21) and (2.22) then imply that the chemical

potential gradients are a linear combination of the relative velocities:

$$-c_m \nabla \mu_m = \sum_{\beta \in \mathbb{M}} \ell_{m\beta} \bar{\boldsymbol{v}}_{\beta}.$$
(2.23)

The phenomenological coefficients can be related to drag coefficients, commonly used in mixture theory [71, 72], by rewriting (2.23) in terms of the relative velocities between the different species:

$$-c_s
abla \mu_s = \sum_{i \in \mathbb{I}} f_{si} \left(\bar{\boldsymbol{v}}_s - \bar{\boldsymbol{v}}_i
ight) + f_{sn} \bar{\boldsymbol{v}}_s,$$
 (2.24)

$$-c_j \nabla \mu_j = \sum_{i \in \mathbb{I}, i \neq j} f_{ji} \left(\bar{\boldsymbol{v}}_j - \bar{\boldsymbol{v}}_i \right) + f_{js} (\bar{\boldsymbol{v}}_j - \bar{\boldsymbol{v}}_s) + f_{jn} \bar{\boldsymbol{v}}_j, \ j \in \mathbb{I}$$
(2.25)

where f_{ab} are the drag coefficients capturing the interaction between the solvent, ionic species and the polymer network. We note that Onsager reciprocal relations require that $f_{mb} = f_{bm}$. Here we have accounted for multi-component transport using the Stefan–Maxwell approach [48, 64] which correctly captures the hydrodynamic drag between different components of the mixture by balancing the friction forces between the different species [3].

A common assumption in mixture theory is that the solute-solute drag can be neglected so that $f_{ij} = 0$ for $i, j \in I$ [38, 71]. The remaining drag coefficients are defined by:

$$f_{sn} = \frac{\nu_s c_s}{k}, \ f_{js} = \frac{k_B T c_j}{\mathcal{D}_j^0}, \ f_{js} + f_{jn} = \frac{k_B T c_j}{\mathcal{D}_j},$$
 (2.26)

where k is related to the permeability of the solvent in the network, \mathcal{D}_j^0 is the diffusion coefficient of the solute in pure solution, while \mathcal{D}_j is the diffusion coefficient of the solute in the gel. For this choice of drag coefficients, the matrix ℓ is:

$$\boldsymbol{\ell} = \begin{bmatrix} \mathbf{d} & -\boldsymbol{f}_s \\ -\boldsymbol{f}_s^T & d_s \end{bmatrix}, \quad \boldsymbol{f}_s = \begin{bmatrix} f_{1s} \\ \vdots \\ f_{Ns} \end{bmatrix}, \quad d_s = \sum_i f_{si} + f_{sn}$$
(2.27)

where ℓ is a symmetric diagonally dominant matrix with positive diagonal entries and hence positive semi-definite in line with Onsager reciprocal relations.

Using (2.24)-(2.26), together with (2.2f) the expressions for the fluxes j_m in terms of the chemical potential gradients are:

$$\boldsymbol{j}_{s} = c_{s} \bar{\boldsymbol{v}}_{s} = -\frac{c_{s} K}{\nu_{s}} \left(\nabla \mu_{s} + \sum_{i \in \mathbb{I}} \frac{\mathcal{D}_{i}}{\mathcal{D}_{i}^{0}} \frac{c_{i}}{c_{s}} \nabla \mu_{i} \right),$$
(2.28)

$$\boldsymbol{j}_{i} = c_{i} \bar{\boldsymbol{v}}_{i} = -\frac{\mathcal{D}_{i} c_{i}}{k_{B} T} \nabla \mu_{i} + \frac{\mathcal{D}_{i} c_{i}}{\mathcal{D}_{i}^{0} c_{s}} \boldsymbol{j}_{s} \quad i \in \mathbb{I},$$
(2.29)

where the coefficient \boldsymbol{K} is defined to be

$$\frac{1}{K} = \frac{1}{k} + \sum_{i \in \mathbb{I}} \frac{k_B T}{\nu_s \mathcal{D}_i^0} \left(1 - \frac{\mathcal{D}_i}{\mathcal{D}_i^0} \right) \frac{c_i}{c_s}.$$
(2.30)

Here K represents the Darcy hydraulic permeability (over dynamic viscosity) of the gel to the solvent and ionic species, whilst k represented the Darcy hydraulic permeability (over dynamic viscosity) to pure solvent.

2.6 The full polyelectrolyte gel model

We now present the full polyelectrolyte gel model in the current configuration. The system of governing equations in the reference configuration is given in Appendix B. We start by using the specific form of the free energy to determine the constitutive equations, and we discuss their physical interpretation in §2.6.1. In §2.6.2 we then collect these equations together with the conservation of mass and momentum equations, definition of electric potential and Gauss' law of electrostatics to describe the full polyelectrolyte gel model in the current configuration.

2.6.1 State equations for prescribed free energy

Substituting the precise form of the free energy Ψ , given in §2.3, into equations (2.19), we obtain the state equations in the reference configuration (see Appendix B). Their form simplifies when expressed in terms of the current configuration. We stress that we now reduce the dependence of the free energy on multiple interfacial energies, and consider only the contributions arising from gradients in the solvent concentration.

The expressions for the microstresses (equations 2.19a,b) are given by

$$\boldsymbol{\xi}_s = \mathbf{F}^{-1} \nabla c_s, \tag{2.31a}$$

$$\boldsymbol{\xi}_n = -c_s \mathbf{F}^{-1} \nabla c_s, \tag{2.31b}$$

These expressions will be utilised in determining the expressions for the solvent chemical potential μ_s and the Cauchy stress **T** in the analysis that follows.

The chemical potential for the solvent (equation 2.19c) is given by

$$\mu_s = \mu_s^0 + \nu_s (p + \Pi_s) + \mu_s^G, \tag{2.32}$$

where μ_s^0 is the reference value for the solvent chemical potential, and the mechanical pressure p, osmotic pressure Π_s and μ_s^G are the contributions to the chemical potential arising from the mechanical stress, mixing and solvent concentration gradient respectively, with Π_s and μ_s^G defined as follows

$$\Pi_{s} = \frac{k_{B}T}{\nu_{s}} \left[\frac{\chi(1 - \nu_{s}c_{s})}{J} + \ln(\nu_{s}c_{s}) + 1 - \sum_{m \in \mathbb{M}} \nu_{s}c_{m} \right],$$
(2.33a)

$$\mu_s^G = -\gamma \nabla^2 c_s, \qquad \qquad (2.33b)$$

and $J = \left(1 - \sum_{m \in \mathbb{M}} \nu_m c_m\right)^{-1}$.

Similarly, the electrochemical potential for the ionic species (equation (2.19d) is given by

$$\mu_{i} = \mu_{i}^{0} + \nu_{i}(p + \Pi_{i}) + z_{i}e\Phi, \ i \in \mathbb{I}$$
(2.34)

where μ_i^0 is the reference value for the ionic chemical potential, the mechanical pressure p and the osmotic pressure Π_i characterise the contributions to the electrochemical potential arising from the mechanical stress and mixing; Π_i is defined by

$$\Pi_{i} = \frac{k_{B}T}{\nu_{i}} \left[-\frac{\chi c_{s}\nu_{i}}{J} + \ln(\nu_{i}c_{i}) + 1 - \sum_{m \in \mathbb{M}} \nu_{i}c_{m} \right], \ i \in \mathbb{I}.$$
(2.35)

Having the form of the solvent chemical potential (2.33a) and ionic species electrochemical potential (2.35) then enables us to determine the solvent and ionic species fluxes, given by (2.28) and (2.29). The multiple dependences of the (electro)chemical potentials on the mobile species concentrations, the gradient of the solvent concentration, the mechanical pressure and the electrostatic potential, as well as the deformation of the gel, means that the solvent and ionic species fluxes are complex expressions. However, as we have shown for the neutral hydrogel [28], it is straightforward to show how these fluxes recover more familiar forms in simplifying limits. Neglecting for now terms due to interfacial energies and the electric field we can consider the following two sublimits. Firstly, we consider $\nu_s C_s \rightarrow \infty$, which corresponds to the limit of large number of solvent molecules. In the current configuration this corresponds to $\nu_s c_s = \phi_s \rightarrow 1$, and $\nu_i c_i = \phi_i \rightarrow 0$ where ϕ_m , $m \in \mathbb{M}$ are the volume fractions of the mobile species in the current configuration. Retaining leading order terms, we find that

$$\boldsymbol{j}_s = -c_s k \nabla p. \tag{2.36}$$

Darcy's law is usually written in the form $v_s - v_n = -k\nabla p$, where k is the hydraulic conductivity of the solvent in the network. The latter has be experimentally estimated (see e.g. [17] and discussion in [2, 28]) and it is found to have the form:

$$k(J) = \frac{\mathcal{D}_s \nu_s}{k_B T} J^{\theta}.$$
(2.37)

where θ is a positive constant. Secondly, we can consider the limit of small number of molecules of mobile species, $\nu_m C_m \to 0$, $m \in \mathbb{M}$, so that in the current configuration $\phi_m \to 0$, $m \in \mathbb{M}$, and $J \to 1$. Retaining leading order terms as $\phi_m \to 0$, and given that $k \to \mathcal{D}_s \nu_s / (k_B T)$, we find that

$$\boldsymbol{j}_{s} = -\mathcal{D}_{s}\left(\nabla c_{s} + \sum_{i \in \mathbb{I}} \frac{\mathcal{D}_{i}}{\mathcal{D}_{i}^{0}} \nabla c_{i}\right),$$
 (2.38)

so that we recover Fick's law of diffusion (first term) and osmotic flux of solvent due to gradients in ionic concentrations (second term). Similar expressions can be found for the flux of ionic species in this limit.

We find the relationship between the electric field and displacement to be

$$\boldsymbol{e} = \frac{1}{\epsilon} \boldsymbol{h} , \qquad (2.39)$$

capturing the standard relationship between electric field and displacement for a linear, homogeneous, isotropic dielectric with instantaneous response to changes in the electric field.

Finally, the Cauchy stress tensor is expressed as follows

$$\mathbf{T} = -p\mathbf{I} + \mathbf{T}_K + \mathbf{T}_M + \mathbf{T}_e, \qquad (2.40a)$$

$$\mathbf{T}_{K} = \gamma \left[\left(\frac{|\nabla c_{s}|^{2}}{2} + c_{s} \nabla^{2} c_{s} \right) \mathbf{I} - \nabla c_{s} \otimes \nabla c_{s} \right],$$
(2.40b)

$$\mathbf{T}_{M} = \epsilon \left[\nabla \Phi \otimes \nabla \Phi - \frac{1}{2} |\nabla \Phi|^{2} \mathbf{I} \right], \qquad (2.40c)$$

$$\mathbf{T}_{e} = \frac{G}{J} \left(\mathbf{B} - \mathbf{I} \right). \tag{2.40d}$$

In determining the Cauchy stress **T** in (2.40a) we used the expression for the microstress $\boldsymbol{\xi}_n$ given by (2.31b). The first term in (2.40a) is the isotropic stress induced by the pressure, while the second term is the elastic stress of the network. The Korteweg (2.40b) \mathbf{T}_K and Maxwell (2.40c) \mathbf{T}_M stress tensors are the stresses generated within the gel due to the formation of internal interfaces (i.e., gradients of the solvent concentration) and the presence of the electric field, respectively.

2.6.2 Full model summary

For ease of reference, we present now the complete model in the current configuration. The conservation equations in the current configuration are given in 2.2 by equations (2.2c), (2.2d), (2.2h), (2.2k) and (2.2l). We use (2.39) to combine equations (2.2k) and (2.2l) via the elimination of the electric field.

The full polyelectrolyte gel model in the current configuration is then given by

$$J = \left(1 - \sum_{m} \nu_m c_m\right)^{-1},$$
(2.41a)

$$\partial_t c_s + \nabla \cdot (c_s \boldsymbol{v}_n) = -\nabla \cdot \boldsymbol{j}_s,$$
 (2.41b)

$$\partial_t c_i + \nabla \cdot (c_i \boldsymbol{v}_n) = -\nabla \cdot \boldsymbol{j}_i, \ i \in \mathbb{I}$$
 (2.41c)

$$\nabla\cdot \mathbf{T} = \mathbf{0}, \tag{2.41d}$$

$$-\epsilon \nabla^2 \Phi = e\left(\sum_{i \in \mathbb{I}} z_i c_i + z_f c_f\right)$$
(2.41e)

where

$$\boldsymbol{j}_{s} = -c_{s}K(c_{s}, c_{i}, J) \left(\nabla \mu_{s} + \sum_{i \in \mathbb{I}} \frac{\mathcal{D}_{i}}{\mathcal{D}_{i}^{0}} \frac{c_{i}}{c_{s}} \nabla \mu_{i} \right),$$
(2.41f)

$$\boldsymbol{j}_{i} = -rac{\mathcal{D}_{i}c_{i}}{k_{B}T}
abla \mu_{i} + rac{\mathcal{D}_{i}c_{i}}{\mathcal{D}_{i}^{0}c_{s}} \boldsymbol{j}_{s}, \ i \in \mathbb{I}$$
 (2.41g)

together with the state equations

$$\mu_{s} = \mu_{s}^{0} + \nu_{s}p + k_{B}T \left[\frac{\chi(1 - \nu_{s}c_{s})}{J} + \ln(\nu_{s}c_{s}) + 1 - \sum_{m \in \mathbb{M}} \nu_{s}c_{m} \right] - \gamma \nabla^{2}c_{s},$$
(2.41h)

$$\mu_{i} = \mu_{i}^{0} + \nu_{i}p + z_{i}e\Phi + k_{B}T \left[-\frac{\chi\nu_{i}c_{s}}{J} + \ln(\nu_{i}c_{i}) + 1 - \sum_{m \in \mathbb{M}}\nu_{i}c_{m} \right], \quad i \in \mathbb{I}$$
(2.41i)

$$\mathbf{T} = -p\mathbf{I} + \mathbf{T}_K + \mathbf{T}_M + \mathbf{T}_e, \qquad (2.41j)$$

$$\mathbf{T}_{K} = \gamma \left[\left(\frac{|\nabla c_{s}|^{2}}{2} + c_{s} \nabla^{2} c_{s} \right) \mathbf{I} - \nabla c_{s} \otimes \nabla c_{s} \right], \qquad (2.41k)$$

$$\mathbf{\Gamma}_{M} = \epsilon \left[\nabla \Phi \otimes \nabla \Phi - \frac{1}{2} \, |\nabla \Phi|^{2} \mathbf{I} \right], \qquad (2.411)$$

$$\mathbf{T}_{e} = \frac{G}{J} \left(\mathbf{B} - \mathbf{I} \right). \qquad (2.41\text{m})$$

where $\boldsymbol{v}_n = \partial \boldsymbol{u}/\partial t + (\boldsymbol{v}_n \cdot \nabla) \boldsymbol{u}$, K is defined by Equations (2.30) and (2.37).

3 Model derivation of an ionic bath

Having derived the model for the polyelectrolyte gel, we now derive the governing equations for flow in the ionic bath adjacent to the gel, following the approach we adopted for the polyelectrolyte gel. The bath is considered as a two phase isotropic mixture with solvent and solute molecules, where the latter are considered to be ionic charges. As the bath has no solid component, we do not have a natural reference configuration. For this reason, the model is derived directly in the current configuration, as standard in the field of mixture theory [4]. The notation for variables in the current configuration that are common to both the polyelectrolyte gel and ionic bath, *e.g.* the ionic concentrations, remains the same. We start by presenting the general model set up in §3.1, together with the kinematic relationships. In §3.2 we state the conservation laws for each component of the mixture, as well as the mixture as a whole. The constitutive properties of the system are specified in §3.3 via the definition of the Helmholtz free energy. The governing and state equations of the system are then derived by using thermodynamics arguments in §3.4. We conclude with a summary of the full model in §3.5, and discuss how our model links to previously proposed models.

3.1 Kinematics

As shown in Figure 1, the ionic bath consists of the solvent and the N freely moving ionic species. Following the same convention as for the gel derivation, we use the subscript s to denote the solvent, and the index i = 1, ..., N to denote the ionic species.

We introduce the tensor **F** to describe the deformation of a volume of mixture $J = \det F$, and the corresponding velocity gradient tensor **L** defined as $\mathbf{L} = \dot{\mathbf{F}}\mathbf{F}^{-1}$. The tensor **L** is commonly decomposed into its symmetric (**D**) and skew symmetric (**W**) parts, *i.e.* $\mathbf{L} = \mathbf{D} + \mathbf{W}$, defined as:

$$\mathbf{D} = \frac{\mathbf{L} + \mathbf{L}^T}{2}, \quad \mathbf{W} = \frac{\mathbf{L} - \mathbf{L}^T}{2}, \tag{3.1}$$

where **D** is their new rate of deformation tensor and **W** is the vorticity or spin tensor.

3.2 Conservation equations

We denote the concentration of the *m*-th species in the solution ($m \in \mathbb{M}$) by c_m , and its velocity by v_m . Conservation of mass for each species is given by Equation (A.3):

$$\frac{\partial c_m}{\partial t} + \nabla \cdot (c_m \boldsymbol{v}_m) = 0, \ m \in \mathbb{M}.$$
(3.2a)

Next we have the no-void condition:

$$1 = \sum_{m \in \mathbb{M}} \nu_m c_m. \tag{3.2b}$$

As in §2.2, we decompose the total flux of the m-th species into an advective component that is carried with the deformation and a diffusive component which represents transport down gradients in chemical potential. This will facilitate the imposition of interfacial conditions, *e.g.* continuity of chemical potential, in §4. We highlight that here the deformation is now determined by the velocity of the mixture v, defined as

$$\boldsymbol{v} = \sum_{m \in \mathbb{M}} \nu_m c_m \boldsymbol{v}_m,$$
 (3.2c)

and the flux of the *m*-th species relative to the mixture velocity is defined as $q_m = c_m (v_m - v)$. Equation (3.2a) is then:

$$\frac{\partial c_m}{\partial t} + \nabla \cdot (c_m \boldsymbol{v}) = -\nabla \cdot \boldsymbol{q}_m, \ m \in \mathbb{M}.$$
(3.2d)

Using the definition of mixture velocity (3.2c), together with the no-void condition (3.2b) we have that the fluxes must satisfy:

$$\sum_{m\in\mathbb{M}}\nu_m \boldsymbol{q}_m = \boldsymbol{0}. \tag{3.2e}$$

Thus in place of \boldsymbol{v}_m we now use \boldsymbol{v} and $\boldsymbol{q}_m, m \in \mathbb{M}$.

Recalling that the material derivative is defined as follows:

$$\frac{Dc_m}{Dt} = \frac{\partial c_m}{\partial t} + \boldsymbol{v} \cdot \nabla c_m, \ m \in \mathbb{M},$$
(3.2f)

equation (3.2d) takes the simple form:

$$\frac{Dc_m}{Dt} + c_m \left(\mathbf{I} : \mathbf{L} \right) = -\nabla \cdot \boldsymbol{q}_m, \ m \in \mathbb{M}$$
(3.2g)

where we have used the identity

$$\nabla \cdot \boldsymbol{v} = \operatorname{tr}(\mathbf{L}) = \mathbf{I} : \mathbf{L}$$
(3.2h)

and the definition of the velocity gradient tensor introduced in §3.1. By multiplying (3.2d) by ν_m , summing over m, and using (3.2b) and (3.2e), we find that the mixture velocity is divergence free:

$$\nabla \cdot \boldsymbol{v} = 0.$$
 (3.2i)

Neglecting the inertia of the mixture (so that viscous effects dominate inertial effects corresponding to low Reynolds number of the mixture), and assuming that the bath is not subject to external forces, conservation of momentum for the mixture is:

$$\nabla \cdot \mathbf{T} = \mathbf{0},\tag{3.2j}$$

where \mathbf{T} is the stress tensor. Following [9, 24], we assume it to be symmetric, which implies balance of internal and external angular momentum. For a more detailed discussion, we refer to [24].

Finally, the relationship between the electric field e and electrostatic potential Φ , and Gauss' law of electrostatics for the electric displacement h are analogous to those for the gel (2.2k)-(2.2l) with the charge density q given by:

$$q = \sum_{i \in \mathbb{I}} e z_i c_i. \tag{3.3}$$

3.3 Free energy

The Helmholtz free energy per unit volume of the mixture (note that in §2.3 the free energies were per unit volume in the reference configuration) is denoted by $\psi = \psi(x, t)$, and has three contributions:

$$\psi = \psi_1 + \psi_2 + \psi_3, \tag{3.4}$$

corresponding to the energy of the electric field (ψ_1) ; the energy of solvent and solutes not interacting with each other (ψ_2) ; and the energy associated with mixing the different component of the mixture (ψ_3) . Note that we have here neglected the interfacial energy as we do not anticipate sharp interfaces and phase separation occurring in the ionic bath. Having discussed the forms of these free energies in detail in §2.3, here we give the specific forms of each contribution. The first energy ψ_1 is

$$\psi_1 = \frac{1}{2\epsilon} \boldsymbol{h} \cdot \boldsymbol{h},$$
 (3.5a)

where ϵ is the permittivity of the mixture. As for the polyelectrolyte gel, the permittivity is dominated by that of the solvent, with little contribution from the mobile phases. For this reason, we consider the permittivity of the both the polyelectrolyte gel and ionic bath to be equal.

The energy density ψ_2 is instead given by:

$$\psi_2 = \sum_{m \in \mathbb{M}} \mu_m^0 c_m, \tag{3.5b}$$

with μ_m^0 as defined in §2.3. Finally the mixing energy of the solvent and ions ψ_3 reads:

$$\psi_3 = k_B T \sum_{m \in \mathbb{M}} c_m \ln \left(c_m \nu_m \right).$$
(3.5c)

3.4 Energy imbalance inequality

Considering a control volume in the current configuration $\mathcal{V}(t)$, the energy imbalance inequality (2.11) is now:

$$\frac{\mathsf{d}}{\mathsf{d}t} \left\{ \int_{\mathcal{V}(t)} \psi \, dv \right\} \le \mathcal{W}(\mathcal{V}(t)) + \mathcal{M}(\mathcal{V}(t)). \tag{3.6}$$

This inequality must hold for all motions which satisfy the no-void (3.2b) and incompressibility (3.2i) constraints. However, since these two constraints are algebraically equivalent, it is sufficient to impose only one of them when using the energy imbalance inequality to derive constitutive relationships for the mixture. We choose to enforce the no-void condition (3.2b) via a Lagrange multiplier. This approach allows the composition variables c_m to be treated as independent and does not require the incompressibility constraint $\nabla \cdot \boldsymbol{v} = \mathbf{I} : \mathbf{L} = 0$ to be enforced during the calculations. Alternative derivations which do enforce the incompressibility constraint, rather than the no-void constraint, can be found in, e.g., [40]. Thus, by using Reynolds' transport theorem and exploiting the relationship (3.2h), the energy imbalance inequality (3.6) can be written as:

$$\int_{\mathcal{V}(t)} \frac{D\psi}{Dt} + \psi\left(\mathbf{I}:\mathbf{L}\right) dv \le \mathcal{W}(\mathcal{V}(t)) + \mathcal{M}(\mathcal{V}(t)).$$
(3.7)

The rate of mass transport \mathcal{M} is analogous to that for the gel, *i.e.* Equation (2.14), accounting for the relationships between the current and reference states given by the identities (2.2a)-(2.2b). We therefore obtain:

$$\mathcal{M}(\mathcal{V}(t)) = \sum_{m \in \mathbb{M}} -\int_{\mathcal{S}(t)} \mu_m \, \boldsymbol{q}_m \cdot \boldsymbol{n} da = \sum_{m \in \mathbb{M}} -\int_{\mathcal{V}(t)} \nabla \cdot (\mu_m \, \boldsymbol{q}_m) \, dv \tag{3.8a}$$

where μ_m is the chemical potential associated with each species in the solution. Similarly, we can derive the rate of electrical and mechanical from (2.12)-(2.13) respectively by moving to the current state (see Appendix C for details of the derivation of equations (3.8b) and (3.8c)):

$$\mathcal{W}_{el}(\mathcal{V}(t)) = -\int_{\mathcal{S}(t)} \Phi\left(\frac{D\boldsymbol{h}}{Dt} + \boldsymbol{h}\left(\boldsymbol{\mathsf{I}}:\boldsymbol{\mathsf{L}}\right) - \boldsymbol{\mathsf{L}}\boldsymbol{h}\right) \cdot \boldsymbol{n}da$$
$$= \int_{\mathcal{V}(t)} \left(\boldsymbol{e}\frac{D\boldsymbol{h}}{Dt} + \left[\left(\boldsymbol{e}\cdot\boldsymbol{h}\right)\boldsymbol{\mathsf{I}} - \boldsymbol{e}\otimes\boldsymbol{h} - \Phi\left(\nabla\cdot\boldsymbol{h}\right)\boldsymbol{\mathsf{I}}\right] : \boldsymbol{\mathsf{L}} - \Phi\frac{Dq}{Dt}\right)dv, \quad (3.8b)$$

$$\mathcal{W}_{mec}(\mathcal{V}(t)) = \int_{\mathcal{S}(t)} \mathbf{T} \boldsymbol{n} \cdot \boldsymbol{v} dA = \int_{\mathcal{V}(t)} \mathbf{T} : \mathbf{L} dv.$$
(3.8c)

DOI 10.20347/WIAS.PREPRINT.2802

Given the definitions (3.8) and following the same steps as in Section 2.4, we rewrite (3.7) as:

$$\frac{D\psi}{Dt} - \boldsymbol{e}\frac{D\boldsymbol{h}}{Dt} + \sum_{i\in\mathbb{I}} \left[\Phi ez_i - \mu_i + \nu_i\lambda\right]\frac{Dc_i}{Dt} + \left(\nu_s\lambda - \mu_s\right)\frac{Dc_s}{Dt} + \left(-\mathbf{T} - (\boldsymbol{e}\cdot\boldsymbol{h})\mathbf{I} + \Phi(\nabla\cdot\boldsymbol{h})\mathbf{I} + \boldsymbol{e}\otimes\boldsymbol{h} + \left(\psi - \sum_{m\in\mathbb{M}}\mu_m c_m\right)\mathbf{I}\right) : \mathbf{L} + \sum_{m\in\mathbb{M}}\nabla\mu_m\cdot\boldsymbol{q}_m \le 0$$
(3.9)

where we have introduced the Lagrange multiplier λ to account for the no-void condition (3.2b). From §3.3, the free energy ψ takes the form $\psi = \psi(c_m, h)$, and inequality (3.9) becomes:

$$\left(\frac{\partial\psi}{\partial\boldsymbol{h}}-\boldsymbol{e}\right)\frac{D\boldsymbol{h}}{Dt}+\sum_{i\in\mathbb{I}}\left[\Phi ez_{i}-\mu_{i}+\nu_{i}\lambda+\frac{\partial\psi}{\partial c_{i}}\right]\frac{Dc_{i}}{Dt}+\left(\nu_{s}\lambda-\mu_{s}+\frac{\partial\psi}{\partial c_{s}}\right)\frac{Dc_{s}}{Dt}+\left(-\mathbf{T}-(\boldsymbol{e}\cdot\boldsymbol{h})\mathbf{I}+\Phi(\nabla\cdot\boldsymbol{h})\mathbf{I}+\boldsymbol{e}\otimes\boldsymbol{h}+\left(\psi-\sum_{m\in\mathbb{M}}\mu_{m}c_{m}\right)\mathbf{I}\right):\mathbf{L}+\sum_{m\in\mathbb{M}}\nabla\mu_{m}\cdot\boldsymbol{q}_{m}\leq0.$$
(3.10)

In the gel, the viscosity of the fluid is captured in the permeability term, *i.e.* via dissipation due to the motion of the solvent with respect to the gel. In the bath, this needs to be accounted for explicitly and we therefore decompose the stress tensor as the sum of an equilibrium and viscous contribution:

$$\mathbf{T} = \mathbf{T}_{equi} + \mathbf{T}_{v}. \tag{3.11}$$

where \mathbf{T}_{equi} is defined as:

$$\mathbf{T}_{equi} = -(\boldsymbol{e} \cdot \boldsymbol{h})\mathbf{I} + \Phi(\nabla \cdot \boldsymbol{h})\mathbf{I} + \boldsymbol{e} \otimes \boldsymbol{h} + \left(\psi - \sum_{m \in \mathbb{M}} \mu_m c_m\right)\mathbf{I}.$$
 (3.12a)

Similarly to the gel, inequality 3.10 is linear in Dh/Dt, Dc_m/Dt , $m \in M$, each of which can be chosen independently at each point x and time t. For the energy imbalance inequality to be always satisfied, we must have that:

$$\mu_s = \frac{\partial \psi}{\partial c_s} + \nu_s \lambda, \qquad (3.12b)$$

$$\mu_{i} = \frac{\partial \psi}{\partial c_{i}} + e\Phi z_{i} + \nu_{i}\lambda, \ i \in \mathbb{I}$$
(3.12c)

$$e = \frac{\partial \psi}{\partial h}.$$
 (3.12d)

The energy imbalance (3.10) then reduces to:

$$-\mathbf{T}_{v}:\mathbf{L}+\sum_{m\in\mathbb{M}}\nabla\,\mu_{m}\cdot\boldsymbol{q}_{m}\leq0.$$
(3.13)

where \mathbf{T}_v and $\nabla \mu_m$ play the role of thermodynamics forces, while \mathbf{L} and \mathbf{q}_m are the corresponding thermodynamics fluxes. In the following section, we consider the irreversible processes associated with mass transport and viscous dissipation, and determine the equations relating the mass fluxes \mathbf{q}_m to the chemical potential gradients $\nabla \mu_m$, and the viscous stress tensor \mathbf{T}_v to the velocity gradient tensor \mathbf{L} .

3.4.1 Governing equations

Given the symmetry of the stress tensor **T** and the fact that \mathbf{T}_{equi} is symmetric, we must have that \mathbf{T}_v is symmetric. We then have that $\mathbf{T} : \mathbf{W} = 0$, so that $\mathbf{L} = \mathbf{D} + \mathbf{W}$ can be substituted by **D** in (3.13). Utilising the definition of the mixture velocity, *i.e.* equation (3.2c), together we the relationship $\mathbf{q}_m = c_m(\mathbf{v}_m - \mathbf{v})$, equation (3.13) can be rewritten as:

$$-\mathbf{T}_{v}:\mathbf{D}+\sum_{m\in\mathbb{M}}c_{m}\left(\nabla\,\mu_{m}-\sum_{\beta\in\mathbb{M}}c_{\beta}\nu_{m}\nabla\,\mu_{\beta}\right)\cdot\boldsymbol{v}_{m}\leq0.$$
(3.14)

Again assuming that we are in the regime of linear non-equilibrium thermodynamics (see §2.5), and considering the additional constraint imposed by *Curie's law*⁵, we arrive at the following set of force-flux relations:

$$\mathbf{T}_{v} = 2\eta \left(\mathbf{D} - \frac{1}{3} (\mathbf{I} : \mathbf{D}) \mathbf{I} \right) + \kappa (\mathbf{I} : \mathbf{D}) \mathbf{I},$$
(3.15)

$$-c_m \left(\nabla \mu_m - \sum_{\beta \in \mathbb{M}} \nu_m c_\beta \nabla \mu_\beta \right) = \sum_{k \in \mathbb{M}} \ell_{km} \boldsymbol{v}_k, \ m \in \mathbb{M}$$
(3.16)

where the matrix of phenomenological coefficients $\boldsymbol{\ell} = [\ell_{ij}]$ must again be symmetric and semipositive definite, while η and κ are positive constants representing the shear viscosity for the mixture and the dilatational viscosity respectively. Note that the latter will not actually play a role as the isotropic component of \mathbf{T}_v will vanish upon strongly imposing the incompressibility condition (3.2i).

As before (see §2.5), we can recover the Stefan–Maxwell type of diffusion [48, 64] by relating the phenomenological coefficients h_{ij} to the drag coefficients commonly used in mixture theory, by rewriting equation (3.16) in terms of the relative velocities between the different phases:

$$-c_m\left(\nabla \mu_m - \sum_{\beta \in \mathbb{M}} \nu_m c_\beta \nabla \mu_\beta\right) = \sum_{k \in \mathbb{M} \setminus \{m\}} f_{km} \left(\boldsymbol{v}_m - \boldsymbol{v}_k\right), m \in \mathbb{M}.$$
 (3.17)

As we did in the gel case, we again consider the drag between ions to be negligible, while $f_{si} = f_{is}$ are defined as in (2.26), so that:

$$-c_{i}\left(\nabla \mu_{i} - \sum_{\beta \in \mathbb{M}} \nu_{i} c_{\beta} \nabla \mu_{\beta}\right) = f_{si}\left(\boldsymbol{v}_{i} - \boldsymbol{v}_{s}\right), i \in \mathbb{I}$$
(3.18a)

$$-c_{s}\left(\nabla \mu_{s} - \sum_{\beta \in \mathbb{M}} \nu_{s} c_{\beta} \nabla \mu_{\beta}\right) = \sum_{i \in \mathbb{I}} f_{is} \left(\boldsymbol{v}_{s} - \boldsymbol{v}_{i}\right).$$
(3.18b)

Analogously to the result in §2.5, for this choice of the fluxes, we have that the matrix ℓ has the same structure as in Eq. (2.27) by setting $f_{mn} = 0$ for all $m \in \mathbb{M}$. Therefore ℓ is still a symmetric and diagonally dominated matrix and hence positive semi-definite.

Note that the system (3.18) is under-determined (their sum is indeed identically zero). This is to be expected as the velocities are not independent of each other but need to satisfy (3.2e). We can therefore use (3.18a) to determine the ionic velocities in terms of v_s , where the latter is defined by (3.2e).

⁵Macroscopic causes can not have more elements of symmetry than the effect they cause (i.e. there can not be any coupling between thermodynamics variable of a different tensorial nature)

We therefore obtain:

$$\boldsymbol{v}_{i} = -\frac{\mathcal{D}_{i}^{0}}{k_{B}T} \left(\nabla \mu_{i} - \sum_{\beta \in \mathbb{M}} \nu_{i} c_{\beta} \nabla \mu_{\beta} \right) + \boldsymbol{v}_{s}, \ i \in \mathbb{I}.$$
(3.19)

Simply subtracting the mixture velocity and multiplying by the ionic concentration c_i we get:

$$\boldsymbol{q}_{i} = -\frac{\mathcal{D}_{i}^{0}c_{i}}{k_{B}T} \left(\nabla \mu_{i} - \sum_{\beta \in \mathbb{M}} \nu_{i}c_{\beta}\nabla \mu_{\beta} \right) + \frac{c_{i}}{c_{s}}\boldsymbol{q}_{s},$$
(3.20a)

$$oldsymbol{q}_s = -\sum_{i\in I}rac{
u_i}{
u_s}oldsymbol{q}_i,$$
 (3.20b)

where (3.20b) is obtained by simply readjusting the terms in (3.2e).

3.4.2 State Equations

Using the definition of the Helmholtz free energy given in §3.3, the constitutive laws (3.12) are as follows:

$$\mu_{s} = \mu_{s}^{0} + \nu_{s}p + k_{B}T \left[\ln \left(\nu_{s}c_{s} \right) + 1 - \sum_{m \in \mathbb{M}} \nu_{s}c_{m} \right],$$
(3.21a)

$$\mu_{i} = \mu_{i}^{0} + \nu_{i}p + k_{B}T \left[\ln \left(\nu_{i}c_{i}\right) + 1 - \sum_{m \in \mathbb{M}} \nu_{i}c_{m} \right] + z_{i}e\Phi, i \in \mathbb{I}.$$
(3.21b)

As before, μ_s is the chemical potential for the solvent and has contributions arising from the mechanical pressure p and mixing. Similarly, μ_i is the electrochemical potential for the ionic species, with the mechanical pressure, mixing and electrostatic potential all contributing. The relationship between the electric field and displacement is again given by

$$h = \epsilon e. \tag{3.22}$$

Finally, the tensor \mathbf{T}_{equi} is found to be

$$\mathbf{T}_{equi} = -p\mathbf{I} + \mathbf{T}_M,\tag{3.23}$$

where

$$T_M = \epsilon \left[\nabla \Phi \otimes \nabla \Phi - \frac{|\nabla \Phi|^2}{2} \mathbf{I} \right], \tag{3.24}$$

is the Maxwell stress tensor (see §2.6.1) due to the presence of the electric field, and the pressure p is defined as:

$$p = \lambda + k_B T \sum_{m \in \mathbb{M}} c_m, \tag{3.25}$$

and we have used the following identity:

$$\psi - \sum_{m} c_{m} \mu_{m} = -\lambda - k_{B}T \sum_{m} c_{m} - \Phi \nabla \cdot \boldsymbol{h} + \frac{|\boldsymbol{h}|^{2}}{2\epsilon}.$$
(3.26)

3.5 The full ionic bath model

The complete model for the bath is given by the following conservation laws presented in Section 3.2:

$$\partial_t c_i + \nabla \cdot (c_i \boldsymbol{v}) = -\nabla \cdot \boldsymbol{q}_i, \quad i \in \mathbb{I},$$
(3.27a)

$$abla \cdot \mathbf{T} = \mathbf{0},$$
 (3.27b)

$$-\epsilon \nabla^2 \Phi = e \sum_{i \in \mathbb{I}} z_i c_i, \qquad (3.27c)$$

where the fluxes are defined by:

$$\boldsymbol{q}_{i} = -\frac{\mathcal{D}_{i}^{0}c_{i}}{k_{B}T} \left(\nabla \mu_{i} - \sum_{\beta \in \mathbb{M}} \nu_{i}c_{\beta}\nabla \mu_{\beta} \right) + \frac{c_{i}}{c_{s}}\boldsymbol{q}_{s},$$
(3.27d)

$$oldsymbol{q}_s = -\sum_{i\in I}rac{
u_ioldsymbol{q}_i}{
u_s},$$
 (3.27e)

and the mixture velocity v satisfies the standard incompressibility condition:

$$\nabla \cdot \boldsymbol{v} = 0. \tag{3.27f}$$

Note that we do not need to account for the governing equation for the solvent concentration c_s , as this is computed using the no-void condition (3.2b):

$$c_s = \frac{1 - \sum_{i \in \mathbb{I}} \nu_i c_i}{\nu_s}.$$
(3.27g)

The model is then completed by specifying the state equations:

$$\mu_s = \mu_s^0 + \nu_s p + k_B T \left[\ln(\nu_s c_s) + 1 - \sum_{m \in \mathbb{M}} \nu_s c_m \right],$$
(3.27h)

$$\mu_{i} = \mu_{i}^{0} + \nu_{i}p + z_{i}e\Phi + k_{B}T\left[\ln(\nu_{i}c_{i}) + 1 - \sum_{m \in \mathbb{M}}\nu_{i}c_{m}\right],$$
(3.27i)

$$\mathbf{T} = -p\mathbf{I} + \mathbf{T}_M + \mathbf{T}_v, \qquad (3.27j)$$

$$\mathbf{\Gamma}_{M} = \epsilon \left| \nabla \Phi \otimes \nabla \Phi - \frac{|\nabla \Phi|^{2}}{2} \mathbf{I} \right|, \qquad (3.27k)$$

$$\mathbf{T}_{v} = \eta \left(
abla oldsymbol{v} +
abla oldsymbol{v}^{T}
ight),$$
 (3.27l)

and proper initial conditions for the concentration of ions c_i . The viscous stress tensor (3.27l) has been simplified from (3.15) by making use of the tensorial form of the incompressibility condition (3.27f), which reads $\mathbf{I} : \mathbf{D} = 0$.

To better understand the phenomena that are driving the flow in the system, we can rearrange the governing equations to show how the flux of the ionic species depends on gradients of the ionic concentration and electrostatic potential. We use (3.27b) and (3.27j)-(3.27l) to obtain the following expression for the pressure gradient:

$$\nabla p = \eta \nabla^2 \boldsymbol{v} + \epsilon \nabla \Phi \nabla^2 \Phi = \eta \nabla^2 \boldsymbol{v} - \sum_{i \in \mathbb{I}} ec_i z_i \nabla \Phi.$$
(3.28)

Equations (3.27h)-(3.27i) are then be used to derive the following relationship between the gradients of the chemical potentials:

$$\sum_{m \in \mathbb{M}} c_m \nabla \mu_m = \eta \nabla^2 \boldsymbol{v}.$$
(3.29)

Using (3.28). and (3.29) the ionic species flux is then:

$$\boldsymbol{q}_{i} = -\frac{\mathcal{D}_{i}^{0}c_{i}}{k_{B}T} \left(\frac{k_{B}T}{c_{i}} \nabla c_{i} - \sum_{m \in \mathbb{M}} k_{B}T\nu_{i}\nabla c_{m} + ez_{i} \left(1 - \frac{\nu_{i}}{z_{i}} \sum_{\beta \in \mathbb{I}} z_{\beta}c_{\beta} \right) \nabla \Phi \right) + \frac{c_{i}}{c_{s}}\boldsymbol{q}_{s}, i \in \mathbb{I}.$$
(3.30)

If we consider the case in which all reference volume ν_m are identically equal to ν and the well known electro-neutral limit, i.e. $\sum_{i \in \mathbb{I}} z_i c_i = 0$, then the above equation simplifies to:

$$\boldsymbol{q}_{i} = -\mathcal{D}_{i}^{0} \left[\underbrace{\nabla c_{i}}_{\text{Fickian diffusion}} + \underbrace{\frac{ez_{i}c_{i}}{k_{B}T} \nabla \Phi}_{\text{Nernst-Planck diffusion}} \right] + \underbrace{\frac{c_{i}}{c_{s}} \boldsymbol{q}_{s}}_{\text{advection}}, i \in \mathbb{I}$$
(3.31)

and we recover the classic Nernst-Planck equation with an additional advection contribution due to the cross diffusion of the mixture components.

4 Interfacial conditions

The behaviour of the polyelectrolyte gel and ionic bath domains are coupled together via specification of interfacial boundary conditions.

We denote the position of the interface *in the current configuration* by Γ , while $[\cdot]^+_{-}$ denotes the jump in the value of a variable across the interface where - and + stand for the limit approaching from the gel and the bath domain respectively. The local velocity of the interface v_{Γ} is equivalent to the normal component of the network velocity v_n . Thus the kinematic boundary condition reads:

$$\boldsymbol{v}_{\Gamma} = (\boldsymbol{v}_n \cdot \boldsymbol{n}) \, \boldsymbol{n},$$
 (4.1a)

where n = n(x, t) is the normal vector to the interface. Consequently, imposing the conservation of mass across the interface and using a pillbox argument gives

$$[c_m \left(\boldsymbol{v}_m - \boldsymbol{v}_\Gamma \right) \cdot \boldsymbol{n}]_{-}^+ = 0. \tag{4.1b}$$

Conservation of momentum leads to the continuity of the normal component of the stress tensor:

$$[\mathbf{T} \cdot \boldsymbol{n}]_{-}^{+} = \boldsymbol{0}. \tag{4.1c}$$

Assuming that there are no surface dipoles or charges on the gel-ionic bath interface we also have continuity of the electrical potential and the displacement field; both follow from pillbox arguments applied to Maxwell's laws.

$$[\Phi]_{-}^{+} = 0, \tag{4.1d}$$

$$[-\epsilon \nabla \Phi \cdot \boldsymbol{n}]_{-}^{+} = 0. \tag{4.1e}$$



Figure 3: Sketch of a gel swelling in a ionic bath with constraints.

We also impose continuity of the chemical potential:

$$[\mu_m]_{-}^{+} = 0. \tag{4.1f}$$

Furthermore, we impose conditions of no interaction of the solvent with the interface:

$$\nabla c_s|_{\Gamma^-} \cdot \boldsymbol{n} = 0. \tag{4.1g}$$

This additional condition becomes necessary (only) on the gel side due to the higher derivative contributions for the concentration of the solvent to the chemical potential in (2.41h).

The governing equations for the gel and ionic bath, together with the coupling conditions given here at the interface, are then complemented with appropriate conditions at domain boundaries. In the following section §5 we now apply the framework to a specific example: a 1D Cartesian geometry.

5 Pattern formation and dynamic fluctuations

We now illustrate the classes of behaviour captured by our model. We consider the constrained collapse (or swelling) of a polyelectrolyte gel with three mobile species: the solvent and two ionic species: c_+ and c_- , with opposite charges, z_+ and z_- , respectively. We model the experimental scenario in which the concentration of ionic species in the ionic solution is controlled by adding salt or pure solvent. We assume all species have the same characteristic molecular volume ν , i.e. $\nu_s = \nu_+ = \nu_- \equiv \nu$ [73]. We specifically consider the case of the constrained swelling and collapse of a gel that is attached to a substrate at z = 0 at one end, while at z = h(t) the gel is in contact with the ionic bath as shown in Figure 3.

For illustrative purposes, we consider the one-dimensional scenario, in which the polyelectrolyte gel undergoes uni-axial deformation due to the uptake or release of solvent. All velocities and fluxes have components in the z direction only, and the dependent variables are functions of z and time t only. This reduction corresponds to the following experimental scenarios [12]. Firstly, that the gel and ionic bath are free to slide along the side walls, corresponding to zero normal component of the network and mixture velocities, and zero tangential stress. Secondly, that the side walls are sufficiently far apart that the influence of the side walls is not felt in the bulk of the polyelectrolyte-ionic bath solution system, the behaviour is one dimensional.

To simplify our analysis, we consider the electroneutral limit, which is justified by the smallness of the Debye length L_d , i.e. the length scale at which the electric field can induce charge separation, relative to size of the gel and the bath (see Table 1). We first discuss the homogeneous equilibrium states obtained when all temporal and spatial derivatives, as well as all fluxes and velocities, are set to zero.

(We highlight that these equilibrium states are naturally electroneutral.) We discuss the dependence of the bifurcation structure of the system on the material and experimental control parameters. We then consider the one-dimensional time-dependent system. We consider the system to be in a pre-swollen state, or 'initial state' (see Fig. 2), and examine the system dynamics as we change the concentration of ionic species in the ionic bath, illustrating how the system transitions between equilibria. Our one-dimensional dynamic simulations predict the formation of a moving depletion fronts in the process of volume phase transition. Furthermore, by varying the salt concentration in the ionic bath, localised phase separated structures emerge within the polyelectrolyte gel and evolve in time and space.

5.1 Reduction to a one-dimensional electroneutral model

In the one-dimensional scenario, the velocity and flux vectors take the form $v = ve_z$, where e_z is a unit vector in the direction of swelling. Moreover, the deformation tensor **F** and the stress tensor **T** in the polyelectrolyte gel are respectively:

$$\mathbf{F} = \begin{bmatrix} \lambda_0 & 0 & 0\\ 0 & \lambda_0 & 0\\ 0 & 0 & \lambda(z,t) \end{bmatrix}, \quad \mathbf{T} = \begin{bmatrix} T_\ell(z,t) & 0 & 0\\ 0 & T_\ell(z,t) & 0\\ 0 & 0 & T(z,t) \end{bmatrix},$$
(5.1)

where λ_0 is a fixed stretch of the network in the x and y directions, and $\lambda(z,t)$ is the axial stretch, while $T_{\ell}(z,t)$ is the lateral stress in the x and y direction while T(z,t) is the stress in the axial direction.

As discussed in the companion paper [27], the electroneutral limit allows us to neglect the left handsides of Equation (2.41e) and (3.27c). In the one-dimensional setting considered here, the resulting equalities

$$z_{-}c_{-} = z_{f}c_{f} + z_{+}c_{+}, \quad z < h(t),$$
 (5.2a)

$$z_{-}c_{-} = z_{+}c_{+}, \qquad z > h(t),$$
 (5.2b)

for the gel and bath models, respectively, can be used to eliminate one of the ionic concentrations in each of the domains, *e.g.* c_{-} can be uniquely defined in terms of the co-ions c_{+} . In addition, the Maxwell contribution to the stress tensor T_{M} in Equations (2.40) can be neglected in the gel.

The electroneutrality relationships (5.2) hold everywhere in the bulk of the gel and bath, but break down near the interface between the two where a small layer, known as Debye layer, develops. Resolving this 'inner layer' via perturbation expansion, starting from the interfacial conditions outlined in §4, we obtain the following conditions at the free interface z = h(t) (see [27] for derivation details):

$$\partial_z c_s(h(t)^-, t) = 0, \tag{5.3a}$$

$$T(h(t)^{-}, t) = 0,$$
 (5.3b)

$$\mu_s(h(t)^-, t) = \mu_s(h(t)^+, t), \tag{5.3c}$$

$$\mu_{\pm}(h(t)^{-}, t) = \mu_{\pm}(h(t)^{+}, t).$$
(5.3d)

At the substrate boundary z = 0 we assume that the gel is attached, and impose

$$v_n = 0. \tag{5.4a}$$

Additionally, as the boundary is impermeable we impose the no-flux condition,

$$j_m = 0, \quad m \in \mathbb{M}. \tag{5.4b}$$

	Meaning	Typical value(s)
k_B	Boltzmann constant	$1.38\times 10^{-23}~{\rm JK}^{-1}$
T	Temperature	298 K
e	Elementary charge	$1.602 imes 10^{-19} \mathrm{C}$
ϵ	Absolute permittivity (same for pure water and gel)	$7\times 10^{-10}~\mathrm{Fm}^{-1}$
ν	Volume per molecule of mobile species	10^{-28} m^3 ([74])
\mathcal{D}_i^0	Diffusivity of mobile ions in pure solvent	$10^{-9} \mathrm{~m^2~s^{-1}}$ ([61])
\mathcal{D}_i	Diffusivity of mobile ions in gel	$\mathcal{D}_i = \mathcal{D}_i^0$
k	Hydraulic permeability of solvent in the network (θ positive constant, here $\theta=0$ as in [28])	$\frac{\mathcal{D}_s}{k_BT}\phi_n^{-\theta}$
\mathcal{D}_{s}	Diffusivity of the solvent in the gel	$\mathcal{D}_s = 0.1 \mathcal{D}_i$
χ	Flory-Huggins Parameter	0.1 - 2.5
C_f	Concentration of fixed charges in the dry gel	$\nu C_f \sim 0.01 - 0.5$
G	shear modulus	10kPa-100kPa
L	Typical length of a gel	0.001-0.01 m
L_d	Characteristic length scale of the Debye layer	$L_d = \sqrt{\frac{\epsilon k_B T \nu}{e^2}} \sim 10^{-10} \ \mathrm{m}$
L_i	Characteristic width of diffuse interfaces	$L_i = \sqrt{\frac{\gamma}{k_B T \nu}}$
γ	Interface stiffness parameter	chosen so that $L_d \ll L_i < L$

Table 1: Physical parameters used in the full dimensional model (2.41) and characteristics length scale of the problem.

To close the system we also impose the "no-preference" condition (4.1g):

$$\frac{\partial c_s}{\partial z} = 0.$$
 (5.4c)

Finally, we specify far-field conditions for the bath as follows

$$c_i \to c_0^i$$
 s.t. $\sum_{i=+,-} z_i c_0^i = 0,$ (5.5a)

$$\Phi \to 0, \quad p \to 0.$$
 (5.5b)

These represent electroneutrality far away from the interface, no external electric field and constant (e.g. atmospheric) pressure, with the constants chosen to be zero in both cases.

Considering the far-field boundary conditions, equation (5.5a), we consider the scenario in which we control the far field concentration of the ions and impose $c_+^{(b)} \rightarrow c_0$.

5.2 Homogeneous equilibrium solutions

We now investigate the homogeneous steady states of the system, and set all the temporal and spatial derivatives, as well as all the fluxes and velocities in (2.41) and (3.27), to zero. We introduce superscripts (g) and (b) to distinguish variables is the gel and bath, respectively, denoting the homogeneous solutions by $(c_s^{(g,b)}, c_+^{(g,b)}, c_-^{(g,b)}, p^{(g,b)}, T^{(g,b)})$.

The homogeneous steady states all satisfy the condition of electro-neutrality (see equations (2.41e) and (3.27c)). In the bath we find $p^{(b)} \equiv 0$, $T^{(b)} \equiv 0$, $\Phi^{(b)} \equiv 0$, $c_+^{(b)} \equiv c_0$ and $c_-^{(b)} \equiv z_+c_0/z_-$. It is straightforward to determine expressions for stress and chemical potential in the gel and bath (see Appendix D). Imposing continuity of chemical potentials and normal stress at the interface, we obtain the following system of non-linear equations in terms of the three unknowns $c_s^{(g)}$, $c_+^{(g)}$ and λ , which depend on the parameters \mathcal{G} , α_f , $\zeta = z_-/z_+$, νc_0 , λ_0 and χ as follows.

$$\mathcal{G}\frac{(\lambda^2 - 1)}{\lambda_0^2 \lambda} + \ln\left(\frac{\nu c_s^{(g)}}{1 - (1 - \zeta^{-1})\nu c_0}\right) + \frac{\chi(1 - c_s^{(g)}\nu) + 1}{\lambda_0^2 \lambda} = 0,$$
(5.6a)

$$\left(c_{+}^{(g)}\right)^{1-\zeta} - \kappa^{1-\zeta} + \frac{\alpha_f}{\lambda_0^2 \lambda} \left(c_{+}^{(g)}\right)^{-\zeta} = 0,$$
 (5.6b)

$$\lambda_0^2 \lambda - \left(1 - \nu \left(c_s^{(g)} + c_+^{(g)} - \frac{\kappa^{1-\zeta}}{\zeta} \left(c_+^{(g)} \right)^{\zeta} \right) \right)^{-1} = 0,$$
 (5.6c)

where

$$\kappa = \kappa(c_s^{(g)}, \lambda; \nu c_0, \lambda_0, \zeta) = \exp\left(\frac{\chi}{\lambda_0^2 \lambda}\right) \left[\frac{\nu c_0 c_s^{(g)}}{1 - (1 - \zeta^{-1}) \nu c_0}\right],\tag{5.7}$$

the parameter $\alpha_f = z_f \nu C_f/z_+$ measures the number of fixed charges per molecule (relative to the valences of the fixed to mobile species) and \mathcal{G} is a dimensionless parameter corresponding to a scaled shear modulus, $\mathcal{G} = G\nu/(k_BT)$. Having determined $c_s^{(g)}$, $c_+^{(g)}$ and λ , it is straightforward to compute $p^{(g)}$, $T^{(g)}$, $\Phi^{(g)}$ and $c_-^{(g)}$ (see Appendix D). Note that Equations (5.6b) is derived from a generalisation

of the standard Donnan equilibrium [13, 37] to our specific problem (see Eq. (D.4a) in Appendix D), where we have an additional exponential contribution in (5.7) due to the mixing energy.

To further reduce the parameter space, we assume $z_+ = -z_-$, so that $\zeta = -1$. Equation (5.6b) can then be solved explicitly:

$$c_{+}^{(g)} = -\frac{\alpha_f}{2\lambda_0^2\lambda} + \sqrt{\left(\frac{\alpha_f}{2\lambda_0^2\lambda}\right)^2 + \frac{c_0^2(c_s^{(g)})^2\nu^2}{\left(1 - 2c_0\nu\right)^2}\exp\left(2\frac{\chi}{\lambda_0^2\lambda}\right)},$$
(5.8)

and we can rewrite the system (5.6) in terms of the two unknowns $c_s^{(g)}$ and λ :

$$0 = \mathcal{G}\frac{\lambda^2 - 1}{\lambda_0^2 \lambda} + \ln \frac{\nu c_s^{(g)}}{1 - 2\nu c_0} + \frac{\chi (1 - c_s^{(g)} \nu) + 1}{\lambda \lambda_0^2},$$
 (5.9a)

$$\frac{\lambda\lambda_0^2 - 1}{\lambda\lambda_0^2} = \nu c_s^{(g)} + 2\sqrt{\left(\frac{\alpha_f}{2\lambda\lambda_0^2}\right)^2 + \left(\frac{\nu c_0\nu c_s^{(g)}}{1 - 2c_0\nu}\right)^2} \exp\left(\frac{2\chi}{\lambda_0^2\lambda}\right).$$
(5.9b)

Equations (5.9) reveal that the behaviour of the system depends on five (dimensionless) parameters α_f , \mathcal{G} , λ_0 , χ and νc_0 . The first two are material parameters. The third reflects a fixed pre-stretch of the network in the x and y directions (see equation (5.1)) and is determined by the experimental setup. While for a given experiment, α_f , \mathcal{G} , λ_0 are fixed, the remaining two parameters can be controlled during the experiment by altering environmental conditions as follows. The Flory-Huggins parameter χ can be manipulated by increasing or lowering the temperature or by adding certain compounds to the bath, such as acetone [53, 73], while the concentration of ions in the bath νc_0 can be set to the desired level by adding salt or pure solvent.

5.2.1 Results

In Figure 4 and 5, we investigate how the equilibrium stretch λ responds to changes of the environment, for different gels and degrees of pre-stretch λ_0 , characterised by triples $(\mathcal{G}, \alpha_f, \lambda_0)$. This amounts to computing the equilibrium manifold defined in the space $(\nu c_0, \chi, \lambda)$ for different choices of $(\mathcal{G}, \alpha_f, \lambda_0)$.

In general, we notice that for small χ ($\chi \sim 0.5$) the gel presents a single, swollen equilibrium i.e. with a large value of λ that remains constant as the salt concentration is increased, see e.g. the blue line for $\chi = 0.5$ in Figure 4a. The degree of swelling λ decreases for larger \mathcal{G} , corresponding to stiffer gels (compare for example figures 4c and 4d). In contrast, for sufficiently large χ , the gel typically stays in the dry state corresponding to small values of λ , for all salt concentrations (determined by νc_0). In Figure 4c, this behaviour is observed for values of χ larger than 0.95. For stiff gels (large \mathcal{G}) and small/or concentrations of fixed charges (small α_f), see Figs. 4a,b,d, values of χ between these extremes show qualitatively the same behaviour with a flat line that shifts to smaller λ (less swollen gels) as χ is increased.

However, for soft gels with high fixed charge concentrations (e.g. Figure 4c) the degree of swelling for intermediate χ values decreases rapidly with increasing salt concentration (see for example the $\chi = 0.85$ contour). Moreover, for a range of lower salt concentrations (set by the value of νc_0) multiple solutions are possible. For example, for $\chi = 0.95$, three solutions for λ exist over almost the full range of νc_0 considered in the Figure 4c. If we start with small νc_0 on the swollen branch i.e. the branch with the largest value of λ , and increase the salt concentration, the degree of swelling will first



Figure 4: Series of equilibrium manifolds as defined by Equations (5.9) for a non pre-stretched ($\lambda_0 = 1$) gel with different mechanical (\mathcal{G}) and electrical (α_f) properties. For the free parameters, i.e. ($\chi, \nu c_0$) we consider the domain [0.01, 2] \times [10⁻⁶, 10^{-2.5}].

decrease slowly, then more rapidly. At a critical bifurcation value of νc_0 this upper branch joins with the lower branch, and for values of νc_0 beyond this bifurcation value, neither of these two branches exist. At the bifurcation point, λ will drop down to the collapse branch, i.e. the branch with the lowest λ value. Once on the collapse branch, the solution stays on the dry branch as the salt concentration is decreased below its bifurcation value, and we observe typical hysteretic behaviour. For a given α_f we find multiple solutions for the stretch for values of \mathcal{G} less than a critical value \mathcal{G}_c .

This behaviour has been observed in the free swelling case [73]. In the constrained case considered here we have the degree of pre-stretch, λ_0 , as an additional parameter. As the value of λ_0 is increased (compare Figure 4 and Figure 5), the range of \mathcal{G} and α_f where multiple solution branches are possible increases. For a given α_f , this corresponds to an increase in the critical value of \mathcal{G}_c , below which multiple solutions are obtained. Thus multiple solution branches and associated hysteretic behaviour are possible for stiffer gels and for lower concentrations of the fixed charges.

Furthermore, by comparing the constrained and the free swelling case directly (see Appendix D.1 for a more detailed discussion), it is possible to show that while in the absence of pre-stretch ($\lambda_0 = 1$) the appearance of multiple solution branches in the constrained case requires softer gels than in the free swelling case, this behaviour can be reversed by considering larger values of λ_0 .

To see this, we compare (5.9) with the corresponding result for the free swelling case (the derivation



Figure 5: Same as in Figure 4 but for a pre-stretch ($\lambda_0 = 5$) gel.

of which is analogous to the constrained case [73]):

$$0 = \mathcal{G}^* \frac{\lambda^{*2} - 1}{\lambda^{*3}} + \ln \frac{c_s^{(g)}\nu}{1 - 2c_0\nu} + \frac{\chi(1 - c_s^{(g)}\nu) + 1}{\lambda^{*3}}$$
(5.10a)

$$\frac{\lambda^{*3} - 1}{\lambda^{*3}} = \nu c_s^{(g)} + 2\sqrt{\left(\frac{\alpha_f}{2\lambda^{*3}}\right)^2 + \left(\frac{\nu c_0 \nu c_s^{(g)}}{1 - 2c_0 \nu}\right)^2 \exp\left(2\frac{\chi}{\lambda^{*3}}\right)},$$
(5.10b)

where \mathcal{G}^* and λ^* correspond to the stiffness and stretch of the swelling gel. If we assume $\lambda, \lambda^* \gg 1$ and drop the -1 in the numerator of the first term in (5.9a) and (5.10a), the solution can be mapped from the constrained to the free case via

$$\lambda_0^2 \lambda = \lambda_*^3, \qquad \mathcal{G}\lambda^2 = \mathcal{G}_*\lambda_*^2, \tag{5.11}$$

which implies that

$$\frac{\mathcal{G}_*}{\mathcal{G}} = \frac{\lambda^{*4}}{\lambda_0^4}.$$
(5.12)

Suppose now we observe multiple solutions for the stretch in the freely swelling gel for values of \mathcal{G}^* less than a critical value \mathcal{G}_c^* . Then, for $\lambda_0 = 1$, we observe that the corresponding critical value of stiffness for the constrained gel is such that $\mathcal{G}_c < \mathcal{G}_c^*$, and multiple solution branches for the stretch appear at softer gel stiffnesses for the constrained case compared with the freely swelling case. If, however, the pre-stretch is much larger so that $\mathcal{G}_c > \mathcal{G}_c^*$, we obtain the opposite behaviour with multiple solution branches observed in the constrained case for stiffer gels compared with the freely swelling case. This agrees with observations in the literature [19, 33] that volume phase transitions in compressed gels occur earlier, e.g. at lower values of the salt concentration, and vice-versa for decompressed (stretched) gels.

5.3 Swelling and collapse dynamics

In the following section §5.3, we present time-dependent simulations of the 1D model, and illustrate how the system transitions between the equilibrium states identified in §5.2. In the analysis that follows, we assume no pre-stretch (i.e. $\lambda_0 = 1$). As in §5.2, we again assume the ionic salt to be monovalent, i.e. $z_+ = -z_- = 1$. Further assuming that the bath is very large (so that small changes in ion concentration due to ion exchange with the gel can be neglected), we see that the bath maintains its equilibrium state, characterised by constant ionic concentrations, $c_+^{(b)} = c_-^{(b)} = c_0$ (see §5.2).

We non-dimensionalise the system as follows

$$\mu_m^* = \frac{\mu_m - \mu_m^0}{k_B T}, \qquad \phi_m = \nu c_m, \qquad \phi_f = \nu c_f, \quad \Phi^* = \frac{\Phi e}{k_B T}, \tag{5.13}$$

$$\mathbf{T}^* = \frac{\mathbf{T}}{G}, \qquad z^* = \frac{z}{L}, \qquad t^* = \frac{t}{\tau},$$
 (5.14)

$$p^* = \frac{p}{G}, \qquad j_m^* = \frac{\nu L}{\mathcal{D}_s} j_m, \qquad \tau = \frac{L^2}{\mathcal{D}_s}, \tag{5.15}$$

so as to focus on the length scale of the gel L and the time scale of the solvent diffusion τ . The resulting dimensionless system of governing equations, together with the boundary and interfacial conditions, are presented in §2 of Celora et al. [7]. In addition to the dimensionless material parameters highlighted in §5.2 (\mathcal{G} and α_f), we now have two additional material parameters, fixed for a given experimental scenario:

$$\mathcal{D}_{\pm}^{*} = \frac{\mathcal{D}_{\pm}}{\mathcal{D}_{s}}, \quad \omega = \sqrt{\frac{\gamma}{\nu_{s}k_{B}TL^{2}}}.$$
 (5.16)

where \mathcal{D}_{\pm}^* are the relative diffusivities of the ions with respect to the solvent and ω is given by the ratio of the interfacial and the gel length scales (see respectively L_i and L in Table 1). In the following simulations we fix the value of these parameters to be $\mathcal{D}_{\pm}^* = 10$ and $\omega = 2.5 \times 10^{-2}$.

5.3.1 Results

We first consider the case of a volume phase transition discussed by Yu et al. [73], who observe good agreement of their free swelling equilibrium solutions with the experiments by Ohmine and Tanaka [53]. In particular, their theory captures the parameter values for which a phase transition occurs. These are, in our notation, $0.98 < \chi < 1.55$, $\mathcal{G} = 1.09 \times 10^{-3}$, $0.02 < \alpha_f < 0.1$, $0 < c_0 \nu < 0.06$. The parameter values in Figure 4 lie in this range, with a tendency towards softer gels or smaller values of χ to compensate for the fact that in the constrained swelling scenarios, volume phase transitions are shifted.

So far, almost all theoretical studies have focussed on equilibrium states. Similarly, experiments have considered the final states as well as those aspects of the dynamics that are slowly evolving. Our model allows us to investigate the whole transient from the very fast dynamics of waves of mobile ions to the extremely slow motion of interfaces between phase-separated regions towards a new equilibrium phase-separated pattern.

We now present some example on the complex dynamics that can be observed by changing the concentration of ions in the bath. Perturbations of the environment the gel is in contact with induce the evolution of the gel the system from one equilibrium state (either swollen or collapsed) shown in Figure 4 to another (collapsed or swollen). As we show in what follow, such dynamics can be



Figure 6: Swelling of a soft ($\mathcal{G} = 10^{-4}$) gel with highly fixed charge ($\alpha_f = 0.1$) in contact with an ionic bath of varying ion concentration. The gel is initially in equilibrium with the bath and $\nu c_0(0^-) = 0.05$; at time t = 0 the concentration of ions in the bath is decreased to $\nu c_0(t_{\infty}) = 10^{-2.75}$. (a) Equilibrium curve for the gel at a fixed $\chi = 0.95$. We highlight the initial and the final solvent fraction in the gel and the bistability region (shaded in red). (b-f) Sequence of snapshots for the distribution of solvent and co-ions volume fraction in the gel at different times and the evolution of the gel size h(t). The spatial variable Z is also rescaled so as to be mapped to a fixed domain, i.e. Z = z/h(t). (g) Evolution of the volume fraction of solvent at the two boundary of the gel, i.e. z = 0 and z = h(t). (h) Phase-plane analysis of the evolution of the gel state at the interface, i.e. z = h(t). Here the curves F_s and F_+ are computed with $\nu c_0 = \nu c_0(t_{\infty})$.

accompanied by phase separation that nucleates at the free surface and forms an interface between solvent-rich and solvent-poor phase that then propagates through the gel.

We start by rearranging (5.8)-(5.9) to define our homogeneous equilibrium curves as:

$$F_s(\phi_s, \phi_+) = \mathcal{G}\frac{\lambda(\phi_s, \phi_+)^2 - 1}{\lambda(\phi_s, \phi_+)} + \ln\frac{\phi_s}{1 - 2\nu c_0} + \frac{\chi(1 - \phi_s) + 1}{\lambda(\phi_s, \phi_+)},$$
(5.17a)

$$F_{+}(\phi_{s},\phi_{+}) = -\sqrt{\left(\frac{\alpha_{f}}{2\lambda(\phi_{s},\phi_{+})}\right)^{2} + \frac{c_{0}^{2}(\phi_{s})^{2}\nu^{2}}{(1-2c_{0}\nu)^{2}}\exp\left(2\frac{\chi}{\lambda(\phi_{s},\phi_{+})}\right)} + \frac{\alpha_{f}}{2\lambda(\phi_{s},\phi_{+})} + \phi_{+},$$
(5.17b)

Berlin 2020

where the stretch is defined by the no void condition:

$$\lambda(\phi_{+},\phi_{s}) = \frac{1+\alpha_{f}}{1-2\phi_{+}-\phi_{s}}.$$
(5.17c)

Note that F_s can also be defined in terms of the chemical potentials of the solvent, as $k_B T \nu^{-1} F_s = \mu_s^{(g)} - \mu_s^{(b)} - \mu_s^G$, where we recall μ_s^G being the contribution of the interfacial energy to the chemical potential of the solvent in the bath.

Homogeneous equilibria then occur when $F_s = F_+ = 0$. As shown in Figure 6, we allow the gel to swell by decreasing the concentration of ions in the bath. In Figure 6a we show the homogeneous equilibrium solvent volume fraction in the gel (for fixed χ , \mathcal{G} and α_f) corresponding to $F_s = F_+ = 0$. There is an interval of values for νc_0 for which system is bi-stable. We choose our initial state to be on the right hand ($\nu c_0(0^-) = 0.05$) side of this region.

At time t the concentration in the bath is decreased so as to drive the gel to a highly swollen state just at the left of the bistable region (as shown in the magnification of the curves $F_s = 0$ and $F_+ = 0$ in Figure 6h, the curves only intersect once and there is only one steady state for the chosen value of $\nu c_0^+ = 10^{-2.75}$). The dynamics of the transition between the two steady states is shown in Figure 6(bf), which shows a sequence of snapshots for the distribution of solvent and mobile ions in the gel, and the evolution of the gel size h(t). Note that the spatial variable is rescaled so that results are mapped onto a fixed domain Z = z/h(t). Initially the solvent diffuses into the gel and the concentration of both solvent and ions is fairly uniform (see the light and dark blue line in Figure 6g approaching as $t \to 10^4$). However, at a later time, near the boundary with the bath, a highly-swollen region forms, hence driving the formation of a front which later propagates in the gel (see Fig. 6d). The front divides two homogeneous states. As analysed in more detail in [7], the solvent (and ionic) volume fraction ahead of the front (from z = 0 to the front location) $\phi_s^{(1)}(\phi_+^{(1)})$ and behind the front (from the location of the front to z=1) $\phi_s^{(2)}$ ($\phi_+^{(2)}$) are determined by a *Maxwell condition* for the co-existence of the two phases. Since the volume fraction of solvent prior to phase separation is greater than $\phi_s^{(1)}$, there is an initial back-flow of solvent from the bulk to the free boundary of the gel (see light blue curve in Figure 6g). When looking at the time evolution of the gel size h(t), we can clearly identify the time at which phase separation occurs as it corresponds to a sharp increase in the rate at which h(t) grows. Such behaviour resembles that observed for neutral gels [28], where phase separation was induced by forcing solvent in the gel. In this case the separation occurs naturally by tuning the concentration of ions in the bath.

To better understand the different time scales in the model, we also focus on a single point in the gel and follow its evolution in the (ϕ_s, ϕ_+) phase plane in Figure Fig. 6h. Starting from the red-star, due to the quick diffusion of the ions in the gel, the system is quickly driven to the manifold $F_+(\phi_s, \phi_+) = 0$ along which the dynamics is slow. Subsequently the system start moving towards the next equilibrium state (identified by the orange star). However in doing so the system has to cross the region where the two equilibrium curves (the light and dark green lines in Figure 6h) get close to each other. In this regime, the contribution of the interfacial energy μ_s^G plays a key role in equilibrating the chemical potential in the bath and in the gel which appears to approach a steady state with $\phi_s \sim 0.7$ (t = 8604, light green dot). However as the solution flattens, the contribution of the interfacial energy μ_s^G decreases up to the point at which this is not sufficient to equilibrate the chemical potential in the bath. At this stage, the system is quickly driven towards its actual homogeneous steady state solution (blue dot in the plane). In doing so the trajectory slightly departs from the light green curve and another quick fast-transition drives the gel to the new, highly swollen steady state.

Another scenario that we can investigate with our phase-field approach is microphase separation. This has been investigated widely in particular through experiments [18, 47], where they have observed



Figure 7: Spinodal decomposition in the bulk of the gel and front propagation induced by perturbing the environmental condition. The gel is initially in equilibrium with the bath ($\nu c_0 = 10^{-4}$) with $\chi = 1.75$. At time t = 0 the concentration of ions in the bath is increased to $\nu c_0 = 5 \times 10^{-2}$ while also χ is increased to $\chi = 2.4$. The other parameters are set to: $\mathcal{G} = 10^{-3}$, $\alpha_f = 0.25$. As in 6 we have rescaled the spatial variable Z = z/h(t).

the initial formation small localised regions of concentrated phases, that eventually develop into a continuous phase with the swollen gel in the minority phase. While previous theoretical studies, for example by Wu et al. [69] concern the equilibrium states and their stability in a 1D, as well as in higher dimensions [70], we can now use our approach to investigate the formation an inhalation of such microphases and look at how this impact the overall dynamics of the gel. As shown in Figure 7, by changing the environmental conditions the gel is exposed to, we can induce phase separation at the free interface, as well as spinodal decomposition in the bulk of the gel. In the simulations shown in Figure 7, the gel is initially in homogeneous equilibrium with ge bath $\mathcal{G} = 10^{-3}$, $\alpha_f = 0.25$, $\chi = 1.75$ and $\nu c_0 = 10^{-4}$. At time t = 0, the ionic concentration in the bath is increased to $\nu c_0 = 5 \times 10^{-2}$ and also χ is increased to $\chi = 2.4$. Perturbations of the highly swollen region of the gel form localised collapsed phases. These coarsen, first quickly, then more slowly as the front propagates into the gel. As spinodal decomposition first onsets in the bulk, the gel partially swells (see Fig. 7f). Subsequently, as the collapsed regions continue to coarsen and front propagates into the gel, the latter collapses.

Interesting but possibly difficult to observed is the higher ion concentration in the localised collapsed phases. As we explain in detail in a 1D companion paper, depending on the parameter setting, various combinations of these scenarios can occur on the route to collapse. For comparison, the parameters have been chosen to be in line with the results presented by Wu et al. [69].

Spinodal decomposition can also occur, even if more rarely, in the case of a swelling experiment. When fine tuning the value of the parameters, as in Figure 8, it is indeed possible to drive the gel to its highly swollen equilibrium state. In doing so, we enter the instability region of the gel (see [7] for more details) thus driving the formation of spikes behind the gel in the less swollen region. We can further compute the lateral stresses experienced by the gel, here given in dimensional units by:

$$T_{\ell}(t,z) = G\left[\frac{\phi_n^2 - 1}{\phi_n} + \frac{\omega^2}{\mathcal{G}}(\partial_z \phi_s)^2\right],$$
(5.18)

recalling that, in the electro-neutral limit the Maxwell stress tensor contribution is negligible.

Interestingly, as shown in Figure 9, we note that the bulk of the gel is initially poorly compressed



Figure 8: (a) Sections of the manifold in Figure 4c for $\chi = 0.8$ (green) and $\chi = 0.95$ (orange line, note that we only show th swollen branch). Starting from a swollen gel (green square in (a)), we are able to drive instabilities in the bulk by increasing χ (from 0.8 to 0.9) and decreasing the concentration of ions in the bath (from 5×10^{-2} to 10^{-5}). The dynamics of spinodal decomposition is illustrated in Figure (b-e). Note that the simulation are interrupted prior to reaching the new equilibrium. The values of \mathcal{G} and α_f are as in Figure 4c.



Figure 9: Time evolution and spatial distribution of the lateral stresses in the gel for simulations in Figure 8.

compared to the highly swollen region ahead of the front (near $Z \sim 1$). The initiation of spinodal decomposition rapidly increases the compressive stress experienced by the bulk of the gel, which might drive the formation of surface instabilities as the one observe by Matsuo and Tanaka [47]. The region of high compressive stresses are alternated by smaller region experiencing stabilising tensile stresses corresponding to the through of the spikes in the gel. The non trivial distribution of the stresses suggest the emergence of more complex pattern that can be investigated by considering a full 2D or 3D geometry.

6 Conclusions and outlook

In this study we have derived a fully time dependent, coupled phase-field model for a polyelectrolyte gel surrounded by an ionic bath. The governing equations for the gel and ionic bath are coupled via consistent jump conditions across the electric double-layer, for which we present an asymptotic analysis in the companion paper [27]. Our derivation is based on linear non-equilibrium thermodynamics

and accounts for multi-component transport of ions and solvent, via a Stefan-Maxwell approach for the flow into and out of an ionic bath. In addition to the non-linear elasticity of the gel, we also account for the free energy of internal interfaces associated with phase separation to capture the transient dynamics of patterns that form during gel swelling and collapse. The resulting comprehensive model for a polyelectrolyte gel in an ionic bath allows investigation into the emerging patterns and their dynamics resulting from the interplay of the underlying physics interacting on multiple time and spatial scales. In particular, we can exploit the model to probe and predict the impact of small environmental changes or stimuli on the structural transitions of the polyelectrolyte gel.

In a first set of investigations we formulate the boundary value problem corresponding to constraining the gel in a one-dimensional setting. We derive the equilibrium manifolds and their bifurcations as a function of the shear modulus of the gel, the concentration of fixed charges of the polyelectrolyte and the Flory-Huggins interaction parameter, and discuss the impact of an applied stretch and changes in the salt concentration in the bath on the bifurcations of the system and the existence of multiple solution branches. Additionally, we present some dynamical simulations of the one-dimensional model reduction, where we resolve the transient dynamics of the gel collapse/swelling. Small changes in salt concentration sets off an initial fast wave in ion concentration that triggers a depletion front which then propagates into the swollen bulk from the free surface where the collapsed phase first appears. Besides resolving this first fast dynamics, our model also allows to describe scenarios for other (slower) salt diffusion regimes and their impact on phase transitions within the gel.

We have further shown that the front propagation can be accompanied with micro- or nanophase separation in the bulk of the gel. Interestingly, we reveal increased ion concentration in the locally collapsed regions. While these initial dynamics may be difficult to experimentally observe, our simulations show that these regions quickly coarsen and give rise to regions of high tensile stresses corresponding to the collapsed phases alternated by regions experiencing compressive forces. We note that in higher dimensions this alternation of tensile and compressive stresses may give rise to instabilities leading to complex patterns as previously observed in experiments, see for example in Tanaka [67].

A more comprehensive analysis of the 1D scenario is presented in the companion paper [7], where we present a stability and phase-plane analysis, to predict, describe and understand the formation of the patterns observed. Even though we are able to identify the signatures of the dynamics that give rise to pattern formation in a polyelectrolyte gel, our numerical and analytical results are currently in 1D only, which limits their experimental replication, given the intrinsic 3D nature of the mechanical stress experienced by the gel. Higher dimensional extensions are part of our ongoing research.

We have also shown that unlike simple hydrogels, by increasing the Flory-Huggins parameter, the gel can be driven to a higher swollen state by changing accordingly also the concentration of ions in the bath. As shown in Figure 8, when properly setting the parameters, this can lead to the development of instabilities in the bulk of a swelling gel. However, while parameter regimes for which spinodal decomposition occur in a collapsing gel can be easily identified, our preliminary results suggest that this occurrence in a one-dimensional swelling experiment may be difficult to observe. The initial onset of instabilities may drive the system into the region of attraction of the collapsed steady state (see discussion in §5.2), hence inverting the behaviour of the gel from swelling to collapsing. This intriguing behaviour suggests the lower branch of the bifurcation to be energetically more stable. We postpone a more rigorous analysis into the intricate balance of the physical mechanisms that are driving these transitions to future work.

Finally, we point out that the framework we have developed, that fully resolves the dynamics of polyelectrolyte gels, paves the way for new emerging fields. For example new scenarios, such as the potential impact of shear flow on the gel can now be investigated, since now we can capture the hydrodynamics of the ionic bath accounting for its mechanical interactions with the gel.

A Conservation of mass equation in current configuration

Here we derive the conservation of mass equation in the current configuration, starting from the corresponding equation in the reference configuration (2.1b).

The integral form of (2.1b) is given by

$$\frac{d}{dt} \int_{\mathcal{V}_R} C_m dV_R = -\int_{\mathcal{S}_R} \boldsymbol{J}_m \cdot \boldsymbol{N} dS_R, \tag{A.1}$$

where \mathcal{V}_R is an arbitrary control volume in the reference configuration, \mathcal{S}_R is the associated surface area with outward unit normal vector N. This integral form can be converted to the current configuration using the relations (2.2), together with Reynolds transport theorem, to give

$$\frac{d}{dt} \int_{\mathcal{V}(t)} \left(\frac{\partial c_m}{\partial t} + \nabla \cdot (c_m \boldsymbol{v}_n) \right) dV = -\int_{\mathcal{S}(t)} \boldsymbol{j_m} \cdot \boldsymbol{n} dS, \tag{A.2}$$

where $c_m = C_m/J$ and $j_m = J^{-1}\mathbf{F}J_m$ are the concentration and the flux in the current configuration, respectively. Here ∇ denotes the gradient with respect to the current state, and $v_n = \partial u/\partial t + (v_n \cdot \nabla)u$ is the network velocity in the current state.

The local balance law in Eulerian coordinates then gives the standard mass conservation law used in the theory of mixtures

$$\frac{\partial c_m}{\partial t} + \nabla \cdot (c_m \boldsymbol{v}_n + \boldsymbol{j}_m) = 0.$$
(A.3)

B Polyelectrolyte gel equations in the reference configuration

The main text gives the governing equations for the polyelectrolyte gel in the current configuration as this largely simplifies the form of the stresses. For completeness, here we present the corresponding governing equations in the reference configuration.

$$J = 1 + \sum_{m} \nu_m C_m, \tag{B.1a}$$

$$\partial_t C_s + \nabla_R \cdot \boldsymbol{J}_s = 0, \tag{B.1b}$$

$$\partial_t C_i + \nabla_R \cdot \boldsymbol{J}_i = 0, \ i \in \mathbb{I},$$
 (B.1c)

$$\nabla_R \cdot \mathbf{T} = \mathbf{0},\tag{B.1d}$$

$$-\epsilon \nabla_R^2 \Phi = e\left(\sum_{i \in \mathbb{I}} z_i C_i + z_f C_f\right),\tag{B.1e}$$

where

$$\boldsymbol{J}_{s} = -K\boldsymbol{\mathsf{C}}^{-1}\left(C_{s}\nabla_{R}\mu_{s} + \sum_{i}\frac{\mathcal{D}_{i}}{\mathcal{D}_{i}^{0}}C_{i}\nabla_{R}\mu_{i}\right),\tag{B.1f}$$

$$\boldsymbol{J}_{i} = -\frac{\mathcal{D}_{i}}{k_{B}T}C_{i}\boldsymbol{\mathsf{C}}^{-1}\nabla_{R}\mu_{i} + \frac{\mathcal{D}_{i}}{\mathcal{D}_{i}^{0}}\frac{C_{i}}{C_{s}}\boldsymbol{J}_{s}, \quad i \in \mathbb{I}$$
(B.1g)

together with the state equations:

$$\boldsymbol{\xi}_s = 2\gamma_1 \, \mathbf{C}^{-1} \, \nabla_R \, C_s - \gamma_3 \, \mathbf{C}^{-1} \, \nabla_R \, J, \qquad (B.1h)$$

$$\boldsymbol{\xi}_J = 2\gamma_2 \, \mathbf{C}^{-1} \, \nabla_R \, J - \gamma_3 \, \mathbf{C}^{-1} \, \nabla_R \, C_s, \qquad (B.1i)$$

$$\begin{split} \mu_{s} &= pv_{s} + \mu_{s}^{0} - \nabla_{R} \cdot \boldsymbol{\xi}_{s} + \frac{\partial \gamma_{1}}{\partial C_{s}} G_{iJ} G_{iM} \frac{\partial C_{s}}{\partial X_{J}} \frac{\partial C_{s}}{\partial X_{M}} \\ &+ \frac{\partial \gamma_{2}}{\partial C_{s}} G_{iJ} G_{iM} \frac{\partial J}{\partial X_{J}} \frac{\partial J}{\partial X_{M}} - \frac{\partial \gamma_{3}}{\partial C_{s}} G_{iJ} G_{iM} \frac{\partial C_{s}}{\partial X_{J}} \frac{\partial J}{\partial X_{M}} \\ &+ k_{B} T \left[\ln \left(\frac{C_{s} v_{s}}{J} \right) + 1 - \frac{C_{s} \nu_{s}}{J} + \frac{\chi (J - C_{s} \nu_{s})}{J^{2}} - \sum_{i} \frac{C_{i} \nu_{s}}{J} \right], \end{split}$$
(B.1j)

$$\mu_{i} = pv_{i} + \mu_{i}^{0} + e\Phi z_{i} + k_{B}T \left[\ln\left(\frac{\nu_{i}C_{i}}{J}\right) + 1 - \sum_{\substack{m=s,1,\dots,N\\m}} \frac{\nu_{i}C_{s}}{J} - \frac{\chi C_{s}\nu_{i}}{J^{2}} \right],$$
(B.1k)

$$\mathbf{S} = -pJ\mathbf{F}^{-T} + \mathbf{S}_K + \mathbf{S}_M + \mathbf{S}_e, \qquad (B.1I)$$
$$\mathbf{S}_e = G\left(\mathbf{F} - \mathbf{F}^{-T}\right), \qquad (B.1m)$$

$$\mathbf{b}_e = G\left(\mathbf{F} - \mathbf{F}^{-1}\right), \qquad (B.1m)$$

$$\mathbf{S}_{M} = -\frac{1}{\epsilon J} \left(\frac{1}{2} |\mathbf{F} \mathbf{H}|^{2} \mathbf{I} - (\mathbf{F} \mathbf{H}) \otimes (\mathbf{F} \mathbf{H}) \right) \mathbf{F}^{-T}, \qquad (B.1n)$$

$$\mathbf{S}_{K}\mathbf{F}^{T} = J\frac{\partial\gamma_{1}}{\partial J}G_{iJ}G_{iM}\frac{\partial C_{s}}{\partial X_{J}}\frac{\partial C_{s}}{\partial X_{M}} - 2\gamma_{1}(\mathbf{F}^{-T}\nabla_{R}C_{s})\otimes(\mathbf{F}^{-T}\nabla_{R}C_{s})$$
$$-J\frac{\partial\gamma_{3}}{\partial J}G_{iJ}G_{iM}\frac{\partial C_{s}}{\partial X_{J}}\frac{\partial J}{\partial X_{M}}\mathbf{I} + 2\gamma_{3}\operatorname{Sym}[(\mathbf{F}^{-T}\nabla_{R}J)\otimes(\mathbf{F}^{-T}\nabla_{R}C_{s})]$$
(B.10)

$$+J\frac{\partial\gamma_2}{\partial J}G_{iJ}G_{iM}\frac{\partial J}{\partial X_J}\frac{\partial J}{\partial X_M}-2\gamma_2(\mathbf{F}^{-T}\nabla_R J)\otimes(\mathbf{F}^{-T}\nabla_R J)-J\nabla_R\cdot\boldsymbol{\xi}_J\mathbf{I},$$

where $\gamma_1 = \gamma/(2J)$, $\gamma_2 = C_s^2 \gamma/(2J^3)$, $\gamma_3 = \gamma C_s J^{-2}$, Sym[·] denotes the symmetric part of a tensor, $\mathbf{C} = \mathbf{F}^T \mathbf{F}$ is the right Cauchy-Green deformation tensor and $\mathbf{G} = \mathbf{F}^{-T}$. Note that in taking the partial derivatives of $\gamma_{1,2,3}$ with respect to C_s and J we consider the latter two to be independent.

To move to the formulation in the current state, we use the following identities:

$$\nabla_{R} \cdot \boldsymbol{\xi}_{s} = \gamma J \nabla \cdot \left(J^{-1} \nabla c_{s} \right)$$

= $\gamma \nabla^{2} c_{s} - \frac{\gamma}{J^{2}} \nabla C_{s} \nabla J + \frac{\gamma C_{s}}{J^{3}} \left| \nabla J \right|^{2},$ (B.2a)

$$\nabla_R \cdot \boldsymbol{\xi}_J = -\gamma J \nabla \cdot \left(\frac{c_s}{J} \nabla c_s\right) \tag{B.2b}$$

$$= -\gamma c_s |\nabla c_s|^2 - \gamma |\nabla c_s|^2 + \frac{\gamma C_s}{J^3} \nabla C_s \nabla J - \frac{\gamma C_s^2}{J^4} |\nabla J|^2,$$

$$J\gamma\nabla c_s\otimes\nabla c_s=2\left(\gamma_1\nabla C_s\otimes\nabla C_s-\gamma_3\mathrm{Sym}\left[\nabla C_s\otimes\nabla J\right]+\gamma_2\nabla J\otimes\nabla J\right),\tag{B.2c}$$

so that the chemical potential simplifies to:

$$\begin{split} \mu_s &= pv_s + \mu_s^0 - \gamma \nabla^2 c_s + k_B T \left[\ln \left(\frac{C_s v_s}{J} \right) + 1 - \frac{C_s \nu_s}{J} \right. \\ &+ \frac{\chi (J - C_s \nu_s)}{J^2} - \sum_i \frac{C_i \nu_s}{J} \right], \end{split} \tag{B.2d}$$

DOI 10.20347/WIAS.PREPRINT.2802

Berlin 2020

and the tensor \mathbf{S}_{K} becomes

$$J^{-1}\mathbf{S}_{K}\mathbf{F}^{T} = \left(\gamma c_{s}|\nabla c_{s}|^{2} + \frac{\gamma}{2}|\nabla c_{s}|^{2}\right)\mathbf{I} - \gamma \nabla c_{s} \otimes \nabla c_{s}.$$
 (B.2e)

C Rate of mechanical and electrical work for ionic bath

Here we give additional details required to move between the first and second expressions for the rate of electric work on a reference volume of the ionic bath in the current state (see equation (3.8b)). Starting from the first line of equation (3.8b) we have

$$\mathcal{W}_{el}(\mathcal{V}(t)) = -\int_{\mathcal{S}(t)} \Phi\left(\frac{D\boldsymbol{h}}{Dt} + \boldsymbol{h}\left(\mathbf{I}:\mathbf{L}\right) - \mathbf{L}\boldsymbol{h}\right) \cdot \boldsymbol{n}da.$$
(C.1a)

Application of the divergence theorem gives:

$$\mathcal{W}_{el}(\mathcal{V}(t)) = -\int_{\mathcal{V}(t)} \nabla \cdot \left(\Phi\left(\frac{D\boldsymbol{h}}{Dt} + \boldsymbol{h}\left(\mathbf{I}:\mathbf{L}\right) - \mathbf{L}\boldsymbol{h}\right) \right) dv$$
(C.1b)

Using Equations (2.2k)-(2.2l) and the following identities:

$$\nabla \cdot \left(\frac{D\boldsymbol{h}}{Dt}\right) = \nabla \cdot \left(\frac{\partial h}{\partial t} + (\boldsymbol{v} \cdot \nabla)\boldsymbol{h}\right) = \frac{\partial \nabla \cdot h}{\partial t} + \sum_{j} \sum_{i} \boldsymbol{v}_{i} \frac{\partial^{2} \boldsymbol{h}_{j}}{\partial x_{i} \partial x_{j}}$$
(C.1c)

$$+\sum_{j}\sum_{i}\frac{\partial \boldsymbol{v}_{i}}{\partial x_{j}}\frac{\partial \boldsymbol{h}_{j}}{\partial x_{i}} = \frac{\partial q}{\partial t} + \sum_{i}\boldsymbol{v}_{i}\frac{\partial}{\partial x_{i}}(\nabla \cdot h) + \nabla \boldsymbol{h}^{T}: \mathbf{L} = \frac{Dq}{Dt} + \nabla \boldsymbol{h}^{T}: \mathbf{L}$$

$$e\mathbf{L}h = \sum_{i} e_{i} \sum_{j} L_{ij}h_{j} = \sum (e_{i}h_{j})L_{ij} = (e \otimes h) : \mathbf{L}$$
 (C.1d)

$$div(\mathbf{L}\boldsymbol{h}) = \sum_{i} \frac{\partial}{\partial x_{i}} \left(\sum_{j} L_{ij} h_{j} \right) = \sum_{i} \sum_{j} \frac{\partial L_{ij}}{\partial x_{i}} h_{j} + \sum_{i} \sum_{j} \frac{\partial h_{j}}{\partial x_{i}} L_{ij}$$
(C.1e)

$$=\sum_{j}\frac{\partial}{\partial x_{j}}\left(\sum_{i}\frac{\partial\nu_{i}}{\partial x_{i}}\right)h_{j}+\nabla\boldsymbol{h}^{T}:\mathbf{L}=\sum_{j}\underbrace{\frac{\partial}{\partial x_{j}}(\mathbf{I}:\mathbf{L})h_{j}}_{\nabla(\mathbf{I}:\mathbf{L})\cdot\boldsymbol{h}}+\nabla\boldsymbol{h}^{T}:\mathbf{L}$$
(C.1f)

the equation reduces to:

$$\mathcal{W}_{el}(\mathcal{V}(t)) = \left(\boldsymbol{e}\frac{D\boldsymbol{h}}{Dt} + \left[\boldsymbol{e}\cdot\boldsymbol{h}\boldsymbol{\mathsf{I}} - \boldsymbol{e}\otimes\boldsymbol{h} - \boldsymbol{\Phi}\nabla\cdot\boldsymbol{h}\boldsymbol{\mathsf{I}}\right] : \boldsymbol{\mathsf{L}} - \boldsymbol{\Phi}\frac{Dq}{Dt}\right)dv, \qquad (C.1g)$$

D Equilibrium solutions

We here compute the homogeneous steady states of a gel in equilibrium with an ionic solution, for the case of two ionic species: c_+ and c_- , with opposite charges, z_+ and z_- , respectively.

In the following, we consider the ionic solution and the gel together, so we introduce superscripts (b) and (g) to distinguish variables that correspond to these two systems, respectively. Starting from the ionic bath, we set all the temporal and spatial derivatives, all fluxes and velocities in (3.27) to zero.

Let us assume that we can control the far field concentration of the ions and impose $c_{+}^{(b)} \rightarrow c_{0}$. Then, from the boundary conditions (5.5), we obtain that:

$$p^{(b)} \equiv 0, \tag{D.1a}$$

$$c_{+}^{(b)} \equiv c_{0},$$
 (D.1b)

$$\Phi^{(b)} \equiv 0, \tag{D.1c}$$

$$c_{-}^{(b)} \equiv -\frac{z_{+}}{z_{-}}c_{0}. \tag{D.1d}$$

Further assuming as in Yu et al. [73] that all species have the same characteristic molecular volume ν , i.e. $\nu_s = \nu_+ = \nu_- \equiv \nu$, the other equilibrium variables in the bath are defined by:

$$T^{(b)} \equiv 0, \tag{D.1e}$$

$$\mu_s^{(b)} = \mu_s^0 + k_B T \ln\left(1 - \left(1 - \frac{z_+}{z_-}\right)\nu c_0\right),\tag{D.1f}$$

$$\mu_{+}^{(b)} = \mu_{+}^{0} + k_{B}T\ln(\nu c_{0}), \tag{D.1g}$$

$$\mu_{-}^{(b)} = \mu_{-}^{0} + k_{B}T \ln\left(-\frac{z_{+}}{z_{-}}\nu c_{0}\right).$$
 (D.1h)

Analogously, we can also derive the set of algebraic equation for the homogeneous steady state in the gel from the system (2.41),

$$\mathbf{T}^{(b)} = -p^{(g)} + rac{G(\lambda^2 - 1)}{J},$$
 (D.2a)

$$0 = z_f c_f + z_+ c_+^{(g)} + z_- c_-^{(g)}$$
(D.2b)

$$\mu_s^{(g)} = p^{(g)}\nu + \mu_s^0 + k_B T \left[\ln(c_s^{(g)}\nu) + \frac{\chi(1 - c_s^{(g)}\nu) + 1}{J} \right],$$
(D.2c)

$$\mu_{\pm}^{(g)} = p^{(g)}\nu + \mu_{\pm}^{0} + z_{\pm}e\Phi^{(g)} + k_{B}T\left[\ln(\nu c_{\pm}^{(g)}) - \frac{\chi c_{s}^{(g)}\nu - 1}{J}\right],$$
 (D.2d)

$$\lambda_0 \lambda^2 = J = \left(1 - \nu \left(c_s^{(g)} + c_+^{(g)} + c_-^{(g)} \right) \right)^{-1}.$$
 (D.2e)

Imposing now the boundary conditions at the free interface, we can connect Equations (D.1) and (D.2) by imposing continuity of chemical potentials and of the stress tensor in the direction normal to the

interface. This leads to:

$$-p^{(g)}\nu = k_B T \left[\ln \left(\frac{\nu c_s^{(g)}}{1 - \left(1 - \frac{z_+}{z_-}\right)\nu c_0} \right) + \frac{\chi (1 - c_s^{(g)}\nu) + 1}{J} \right],$$
(D.3a)

$$-p^{(g)}\nu = z_{+}e\Phi^{(g)} + k_{B}T\left[\ln\frac{c_{+}^{(g)}}{c_{0}} - \frac{\chi c_{s}^{(g)}\nu - 1}{J}\right],$$
 (D.3b)

$$-p^{(g)}\nu = z_{-}e\Phi^{(g)} + k_{B}T\left[\ln\left(-\frac{z_{-}c_{-}^{(g)}}{z_{+}c_{0}}\right) - \frac{\chi c_{s}^{(g)}\nu - 1}{J}\right],$$
 (D.3c)

$$-z_{-}c_{-}^{(g)} = z_{f}c_{f} + z_{+}c_{+}^{(g)},$$
(D.3d)

$$p^{(g)} = \frac{G\left(\lambda^2 - 1\right)}{\lambda_0^2 \lambda},$$
 (D.3e)

$$\lambda_0^2 \lambda = \left(1 - \nu \left(c_s^{(g)} + c_+^{(g)} + c_-^{(g)} \right) \right)^{-1}.$$
 (D.3f)

Subtracting Equations (D.3b) and (D.3c), and subtracting (D.3a) from both (D.3b) and (D.3c), we obtain the following relation between the electric potential Φ and the ionic concentrations:

$$c_{-}^{(g)} = -\frac{z_{+}}{z_{-}} \left[\kappa\right]^{1-\frac{z_{-}}{z_{+}}} \left(c_{+}^{(g)}\right)^{\frac{z_{-}}{z_{+}}}, \tag{D.4a}$$

$$\Phi^{(g)} = \frac{k_B T}{e z_+} \ln\left(\frac{\kappa}{c_s^g}\right),\tag{D.4b}$$

where

$$\kappa = \kappa \left(c_s^{(g)}, \lambda; \nu c_0, \lambda_0, \frac{z_+}{z_-} \right) = \exp\left(\frac{\chi}{\lambda_0^2 \lambda}\right) \left[\frac{\nu c_0 c_s^{(g)}}{1 - \left(1 - \frac{z_+}{z_-}\right) \nu c_0} \right].$$
(D.4c)

Note that Equations (D.4a) is a generalisation of the standard Donnan Equilibrium [13, 37] to our specific problem, where the additional exponential contribution in (D.4c) due to the mixing energy as to be considered. Using (D.4) to simplify the system (D.3), the latter reduces to:

$$\mathcal{G}\frac{(\lambda^2 - 1)}{\lambda_0^2 \lambda} + \ln\left(\frac{\nu c_s^{(g)}}{1 - (1 - \zeta^{-1})\nu c_0}\right) + \frac{\chi(1 - c_s^{(g)}\nu) + 1}{\lambda_0^2 \lambda} = 0,$$
(D.5a)

$$c_{+}^{(g)}\Big)^{1-\zeta} - \kappa^{1-\zeta} + \frac{\alpha_f}{\lambda_0^2 \lambda} \left(c_{+}^{(g)}\right)^{-\zeta} = 0,$$
 (D.5b)

$$\lambda_0^2 \lambda - \left(1 - \nu \left(c_s^{(g)} + c_+^{(g)} - \frac{\kappa^{1-\zeta}}{\zeta} \left(c_+^{(g)} \right)^{\zeta} \right) \right)^{-1} = 0.$$
 (D.5c)

where \mathcal{G} is a positive non-dimensional parameter corresponding to a scaled version of shear modulus, $\mathcal{G} = G\nu/(k_BT)$, $\alpha_f = z_f \nu C_f/z_+$ measures the number of fixed charges per molecule (relative to the valences of the fixed to mobile species), and $\zeta = z_-/z_+$. As discussed in the main text (see §5.2), we can further simplify the above system by assuming $z_+ = z_-$ to obtain Eq. (5.9).

D.1 Free-Swelling.

For the free swelling case the deformation tensor $\mathbf{F} = \lambda \mathbf{I}$ so that $\mathbf{B} = \lambda^2 \mathbf{I}$. Similarly to (D.3) we obtain here:

$$-p\nu = k_B T \left[\ln \frac{\nu c_s^{(g)}}{1 - 2\nu c_0} + \frac{\chi (1 - c_s^{(g)} \nu)}{J} \right],$$
 (D.6a)

$$-p\nu = \pm e\Delta\Phi + k_B T \left[\ln \frac{c_{\pm}^{(g)}}{c_0} - \frac{\chi c_s^{(g)} \nu}{J} \right], \tag{D.6b}$$

$$c_{-}^{(g)} = z_f c_f + c_{+}^{(g)}, \tag{D.6c}$$

$$p = \frac{G\left(\lambda^2 - 1\right)\mathbf{I}}{\lambda^3},\tag{D.6d}$$

$$\lambda^{3} = \left(1 - \nu \left(c_{s}^{(g)} + c_{+}^{(g)} + c_{-}^{(g)}\right)\right)^{-1},$$
(D.6e)

together with the relationship between the electric potential and the ionic concentrations:

$$\Phi = \frac{k_B T}{2e} \ln \frac{c_-^{(g)}}{c_+^{(g)}}.$$
 (D.7)

while the concentrations c_+ and c_- are given now by:

$$c_{-}^{(g)} = \frac{c_0 c_s^{(g)} \nu}{1 - 2c_0 \nu} \exp\left(\frac{e\Delta\Phi}{k_B T} + \frac{\chi}{J}\right),\tag{D.8a}$$

$$c_{+}^{(g)} = \frac{c_0 c_s \nu}{1 - 2c_0 \nu} \exp\left(-\frac{e\Delta\Phi}{k_B T} + \frac{\chi}{J}\right). \tag{D.8b}$$

which implies that:

$$c_{+}^{(g)}c_{-}^{(g)} = \frac{c_{0}^{2}(c_{s}^{(g)})^{2}\nu^{2}}{\left(1 - 2c_{0}\nu\right)^{2}}\exp\left(\frac{2\chi}{J}\right).$$
(D.9)

Combining the above with the electro-neutrality condition (D.2b), we can compute an expression for the equilibrium value of the ionic concentrations:

$$c_{\pm}^{(g)} = \mp \frac{z_f c_f}{2} + \sqrt{\left(\frac{z_f c_f}{2}\right)^2 + \frac{c_0^2 (c_s^{(g)})^2 \nu^2}{\left(1 - 2c_0 \nu\right)^2} \exp\left(2\frac{\chi}{J}\right)},$$
 (D.10)

from which it can be seen that the equilibrium solution $(c_s^{(g)}, \lambda) = (c_s^*, \lambda^*)$ is implicitly defined by the system of algebraic equations:

$$0 = \mathcal{G}^* \frac{\lambda^{*2} - 1}{\lambda^{*3}} + \ln \frac{c_s^* \nu}{1 - 2c_0 \nu} + \frac{\chi (1 - c_s^* \nu) + 1}{\lambda^{*3}}$$
(D.11a)

$$0 = \nu c_s^* + 2\sqrt{\left(\frac{\alpha_f}{2\lambda^{*3}}\right)^2 + \frac{c_0^2 c_s^{*2} \nu^2}{\left(1 - 2c_0 \nu\right)^2} \exp\left(2\frac{\chi}{\lambda^{*3}}\right)} - \frac{\lambda^{*3} - 1}{\lambda^{*3}},$$
 (D.11b)

where \mathcal{G}^* is the stiffness of the free swelling gel.

DOI 10.20347/WIAS.PREPRINT.2802

References

- L. Anand. A thermo-mechanically-coupled theory accounting for hydrogen diffusion and large elasticâĂŞviscoplastic deformations of metals. *International Journal of Solids and Structures*, 48(6):962 – 971, 2011.
- [2] T. Bertrand, J. Peixinho, S. Mukhopadhyay, and C. W. MacMinn. Dynamics of swelling and drying in a spherical gel. *Physical Review Applied*, 6(6):064010, 2016.
- [3] D. Bothe and P.-E. Druet. On the structure of continuum thermodynamical diffusion fluxes a novel closure scheme and its relation to the maxwell-stefan and the fick-onsager approach, 2020.
- [4] R. M. Bowen. Theory of mixtures in continuum physics. *Mixtures and Electromagnetic Field Theories*, 3, 1976.
- [5] C. P. Brangwynne, P. Tompa, and R. V. Pappu. Polymer physics of intracellular phase transitions. *Nature Physics*, 11:899–904, 2015.
- [6] D. Buenger, F. Topuz, and J. Groll. Hydrogels in sensing applications, dec 2012.
- [7] G. L. Celora, M. G. Hennessy, A. Münch, S. L. Waters, and B. Wagner. Spinodal decomposition and collapse of a polyelectrolyte gel. *Submitted*, 2020.
- [8] S. Chaterji, I. K. Kwon, and K. Park. Smart polymeric gels: Redefining the limits of biomedical devices, aug 2007.
- [9] B. D. Coleman and W. Noll. The thermodynamics of elastic materials with heat conduction and viscosity. *Archive for Rational Mechanics and Analysis*, 13(1):167–178, dec 1963.
- [10] M. S. Dimitriyev, Y.-W. Chang, P. M. Goldbart, and A. Fernández-Nieves. Swelling thermodynamics and phase transitions of polymer gels. *Nano Futures*, 3(4):042001, oct 2019.
- [11] A. Dobrynin. Theory and simulations of charged polymers: From solution properties to polymeric nanomaterials. *Current Opinion in Colloid & Interface Science*, 13(6):376–388, 2008.
- [12] M. Doi. Gel dynamics. Journal of the Physical Society of Japan, 78(5):052001, 2009.
- [13] F. G. Donnan. The Theory of Membrane Equilibria. Chemical Reviews, 1(1):73-90, 1924.
- [14] W. Dreyer, C. Guhlke, and R. Müller. Modeling of electrochemical double layers in thermodynamic non-equilibrium. *Physical Chemistry Chemical Physics*, 17(40):27176–27194, 2015.
- [15] A. Drozdov. Swelling of ph-responsive cationic gels: Constitutive modeling and structureâĂŞproperty relations. International Journal of Solids and Structures, 64-65:176 – 190, 2015.
- [16] A. D. Drozdov, J. deClaville Christiansen, and C.-G. Sanporean. Inhomogeneous swelling of ph-responsive gels. *International Journal of Solids and Structures*, 87:11 – 25, 2016.
- [17] A. D. Drozdov, A. A. Papadimitriou, J. H. Liely, and C. G. Sanporean. Constitutive equations for the kinetics of swelling of hydrogels. *Mechanics of Materials*, 2016.
- [18] K. Dusek and D. Patterson. Transition in swollen polymer networks induced by intramolecular condensation. Journal of Polymer Science Part A-2: Polymer Physics, 6(7):1209–1216, 1968.

- [19] M. Dušková-Smrčková and K. Dušek. How to Force Polymer Gels to Show Volume Phase Transitions. ACS Macro Letters, 8(3):272–278, 2019.
- [20] L. G. E., S. P. S., V. Dominic, W. S. L., and G. Alain. Is the donnan effect sufficient to explain swelling in brain tissue slices. J. R. Soc. Interface., page 1120140123, 2014.
- [21] A. Estévez-Torres and D. Baigl. DNA compaction: Fundamentals and applications. Soft Matter, 7(15):6746, 2011.
- [22] P. J. Flory. Thermodynamics of high polymer solutions. *The Journal of Chemical Physics*, 10(1):51–61, 1942.
- [23] H. Garcke, B. Nestler, and B. Stinner. A diffuse interface model for alloys with multiple components and phases. SIAM Journal on Applied Mathematics, 2004.
- [24] S. R. d. Groot. Non-equilibrium thermodynamics. North-Holland series in physics. North-Holland, Amsterdam, 1962.
- [25] M. E. Gurtin. Generalized ginzburg-landau and cahn-hilliard equations based on a microforce balance. *Physica D: Nonlinear Phenomena*, 92(3):178 – 192, 1996.
- [26] M. E. Gurtin, E. Fried, and L. Anand. The Mechanics and Thermodynamics of Continua. Cambridge University Press, 2010.
- [27] M. G. Hennessy, G. Celora, A. Münch, B. Wagner, and S. Waters. Asymptotic derivation of jump conditions across a thin debye layer for a polyelectrolyte gel. *Submitted*, 2020.
- [28] M. G. Hennessy, A. Münch, and B. Wagner. Phase separation in swelling and deswelling hydrogels with a free boundary. *Phys. Rev. E*, 101:032501, Mar 2020.
- [29] W. Hong. Continuum Models of Stimuli-responsive Gels, pages 165–196. Springer Berlin Heidelberg, Berlin, Heidelberg, 2012.
- [30] W. Hong and X. Wang. A phase-field model for systems with coupled large deformation and mass transport. *Journal of the Mechanics and Physics of Solids*, 61(6):1281 – 1294, 2013.
- [31] W. Hong, X. Zhao, and Z. Suo. Large deformation and electrochemistry of polyelectrolyte gels. *Journal of the Mechanics and Physics of Solids*, 58(4):558–577, apr 2010.
- [32] F. Horkay, I. Tasaki, and P. J. Basser. Effect of monovalent-divalent cation exchange on the swelling of polyacrylate hydrogels in physiological salt solutions. *Biomacromolecules*, 2(1):195– 199, 2001.
- [33] F. Horkay, I. Tasaki, and P. J. Basser. Effect of Monovalent-Divalent Cation Exchange on the Swelling of Polyacrylate Hydrogels in Physiological Salt Solutions. *Biomacromolecules*, 2(1):195– 199, 2001.
- [34] J. Hua, M. K. Mitra, and M. Muthukumar. Theory of volume transition in polyelectrolyte gels with charge regularization. *The Journal of Chemical Physics*, 136(13):134901, 2012.
- [35] J. Hua, M. K. Mitra, and M. Muthukumar. Theory of volume transition in polyelectrolyte gels with charge regularization. *Journal of Chemical Physics*, 136(13):134901, apr 2012.

- [36] M. L. Huggins. Some properties of solutions of long-chain compounds. The Journal of Physical Chemistry, 46(1):151–158, 1942.
- [37] J. M. Huyghe and J. D. Janssen. Quadriphasic mechanics of swelling incompressible porous media. *International Journal of Engineering Science*, 35(8):793–802, 1997.
- [38] A. Katchalsky and P. Curran. *Nonequilibrium thermodynamics in biophysics*. Books in Biophysics. Harvard University Press, 1965.
- [39] A. R. Khokhlov and E. Y. Kramarenko. Weakly charged polyelectrolytes: Collapse induced by extra ionization. *Macromolecules*, 29(2):681–685, 1996.
- [40] J. Kim and J. Lowengrub. Phase field modeling and simulation of three-phase flows. Interfaces and Free Boundaries, 7(4):435–466, 2005.
- [41] R. Krishna and J. Wesselingh. The maxwell-stefan approach to mass transfer. Chemical Engineering Science, 52(6):861 – 911, 1997.
- [42] H. J. Kwon, Y. Osada, and J. P. Gong. Polyelectrolyte gels-fundamentals and applications. *Polymer Journal*, 38(12):1211–1219, nov 2006.
- [43] H. J. Kwon, K. Yasuda, J. P. Gong, and Y. O. M. Research. Polyelectrolyte hydrogels for replacement and regeneration of biological tissues. *Macromolecular Research*, 22:227–235, 2014.
- [44] F. LarchAl and J. Cahn. The interactions of composition and stress in crystalline solids. Acta Metallurgica, 33(3):331 – 357, 1985.
- [45] G. Lebon, D. Jou, and C.-V. JosÃI. Understanding Non-Equilibrium Thermodynamics. Springer-Verlag Berlin Heidelberg, 01 2008.
- [46] M. P. Lutolf and J. A. Hubbell. Synthetic biomaterials as instructive extracellular microenvironments for morphogenesis in tissue engineering, jan 2005.
- [47] E. S. Matsuo and T. Tanaka. Patterns in shrinking gels. Nature, 358(6386):482–485, 1992.
- [48] J. C. Maxwell. Iv. on the dynamical theory of gases. Phil. Trans. R. Soc., 157:49–88, 1867.
- [49] J. L. Mccoy and M. Muthukumar. Dynamic light scattering studies of ionic and nonionic polymer gels with continuous and discontinuous volume transitions. *Journal of Polymer Science Part B: Polymer Physics*, 48(21):2193–2206, 2010.
- [50] Y. Mori, H. Chen, C. Micek, and M.-C. Calderer. A dynamic model of polyelectrolyte gels. SIAM Journal on Applied Mathematics, 73(1):104–133, 2013.
- [51] M. Mussel and F. Horkay. Experimental Evidence for Universal Behavior of Ion-Induced Volume Phase Transition in Sodium Polyacrylate Gels. *The Journal of Physical Chemistry Letters*, 10(24):7831–7835, 2019.
- [52] C. Ning, Z. Zhou, G. Tan, Y. Zhu, and C. Mao. Electroactive polymers for tissue regeneration: Developments and perspectives, jun 2018.
- [53] I. Ohmine and T. Tanaka. Salt effects on the phase transition of ionic gels. The Journal of Chemical Physics, 77(11):5725–5729, dec 1982.

- [54] L. Onsager. Reciprocal relations in irreversible processes. i. Phys. Rev., 37:405-426, Feb 1931.
- [55] A. Onuki and S. Puri. Spinodal decomposition in gels. Physical Review E, 1998.
- [56] K. R. Rajagopal and A. R. Srinivasa. On thermomechanical restrictions of continua. Proc. R. Soc. Lond. A., 460:631âĂŞ651, 2004.
- [57] D. Roshal, O. Konevtsova, A. Losdorfer Bozic, and et al. ph-induced morphological changes of proteinaceous viral shells. *Scientific Reports*, 9:5341, 2019.
- [58] K. A. Rosowski, T. Sai, E. Vidal-Henriquez, D. Zwicker, R. W. Style, and E. R. Dufresne. Elastic ripening and inhibition of liquid–liquid phase separation. *Nature Physics*, 16(4):422–425, 2020.
- [59] K. A. Rosowski, E. Vidal-Henriquez, D. Zwicker, R. W. Style, and E. R. Dufresne. Elastic stresses reverse Ostwald ripening. *Soft Matter*, 16(25):5892–5897, 2020.
- [60] T. Roubíček. Incompressible ionized fluid mixtures. Continuum Mechanics and Thermodynamics, 17(7):493–509, 2006.
- [61] T. K. Sherwood, R. L. Pigford, and C. R. Wilke. *Mass transfer*. McGraw-Hill Book Co, New York, 1975.
- [62] M. Shibayama. Spatial inhomogeneity and dynamic fluctuations of polymer gels. Macromolecular Chemistry and Physics, 199(1):1–30, 1998.
- [63] C. E. Sing, J. W. Zwanikken, and M. Olvera de la Cruz. Effect of ionâĂŞion correlations on polyelectrolyte gel collapse and reentrant swelling. *Macromolecules*, 46(12):5053–5065, 2013.
- [64] J. Stefan. über das gleichgewicht und die bewegung insbesondere die diffusion von gasgemengen. Sitzungsber. Akad. Wiss. Wien, 63(2):63–124, 1871.
- [65] M. A. Stuart, W. T. Huck, J. Genzer, M. Müller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, and S. Minko. Emerging applications of stimuli-responsive polymer materials. *Nature Materials*, 9(2):101–113, 2010.
- [66] R. W. Style, T. Sai, N. Fanelli, M. Ijavi, K. Smith-Mannschott, Q. Xu, L. A. Wilen, and E. R. Dufresne. Liquid Phase Separation in an Elastic Network. *Physical Review X*, 8(1):011028, 2018.
- [67] T. Tanaka. Collapse of gels and the critical endpoint. Phys. Rev. Lett., 40:820-823, Mar 1978.
- [68] T. Tanaka, S.-T. Sun, Y. Hirokawa, S. Katayama, J. Kucera, Y. Hirose, and T. Amiya. Mechanical instability of gels at the phase transition. *Nature*, 325(6107):796–798, Feb. 1987.
- [69] K.-A. Wu, P. K. Jha, and M. O. de la Cruz. Control of Nanophases in Polyelectrolyte Gels by Salt Addition. *Macromolecules*, 43(21):9160–9167, 2010.
- [70] K.-A. Wu, P. K. Jha, and M. Olvera de la Cruz. Pattern Selection in Polyelectrolyte Gels by Nonlinear Elasticity. *Macromolecules*, 45(16):6652–6657, 2012.
- [71] S.-L. Xue, B. Li, X.-Q. Feng, and H. Gao. A non-equilibrium thermodynamic model for tumor extracellular matrix with enzymatic degradation. *Journal of the Mechanics and Physics of Solids*, 104:32 – 56, 2017.

- [72] S.-L. Xue, S.-Z. Lin, B. Li, and X.-Q. Feng. A nonlinear poroelastic theory of solid tumors with glycosaminoglycan swelling. *Journal of Theoretical Biology*, 433:49 56, 2017.
- [73] Y. Yu, C. M. Landis, and R. Huang. Salt-induced swelling and volume phase transition of polyelectrolyte gels. *Journal of Applied Mechanics*, 84(5):051005, 2017.
- [74] Y. Yu, C. M. Landis, and R. Huang. Salt-induced swelling and volume phase transition of polyelectrolyte gels. *Journal of Applied Mechanics*, 84(5):051005, 2017.
- [75] R. Zandi, B. Dragnea, A. Travesset, and R. Podgornik. On virus growth and form. *Physics Reports*, 847:1–102, 2020.
- [76] H. Zhang, M. Dehghany, and Y. Hu. Kinetics of polyelectrolyte gels. *Journal of Applied Mechanics*, 87(6), 2020.
- [77] A. Y. Zubarev, F. A. Blyakhman, G. H. Pollack, P. Gusev, and A. P. Safronov. Self-Similar Wave of Swelling/Collapse Phase Transition along Polyelectrolyte Gel. *Macromolecular Theory and Simulations*, 13(8):697–701, 2004.