A dynamic model of polyelectrolyte gels

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Haoran Chen

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Yoichiro Mori, Advisor

Maria-Carme Calderer, Co-advisor

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Abstract

We derive a model that couples mechanical and electrochemical effects of polyelectrolyte gels. The gel is assumed to be immersed in a fluid domain. As the gel swells and de-swells, the gel-fluid interface can move. Our model consists of a system of partial differential equations for mass and linear momentum balance of the polymer and fluid components of the gel, the Navier-Stokes equations in the surrounding fluid domain, and the Poisson-Nernst-Planck equations for the ionic concentrations on the whole domain. These are supplemented by a novel and general class of boundary conditions expressing mass and linear momentum balance across the moving gel-fluid interface. A salient feature of our model is that it satisfies a free energy dissipation identity, in accordance with the second law of thermodynamics. We also apply Onsager's variational principle to derive the dynamic equations. The linear stability calculation reveals some interesting features of mechanical gel and polyelectrolyte gel. Particularly, in a one-dimensional analysis of two ion species system, we find how the global exponential decay rate is associated with gel's and ions' intrinsic decay rates. Lastly, we present some simulation results of the one dimensional dynamic model, for which the asymptotic behavior matches with the theoratical calculations.

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Chapter 1

Introduction

Gels are crosslinked, three dimensional polymer networks that absorb solvent and swell without dissolution [19, 20, 13, 37, 2]. Some gels can experience large changes in volume in response to small changes in various environmental parameters including temperature, pH or the ionic composition of the solvent [35]. In some gels, this change is discontinuous with respect to changes in the environmental parameter. This is the volume phase transition, first described in [36]. One interesting feature of the volume phase transition is that it exhibits hysteresis, a feature that distinguishes it from the familiar liquid-gas phase transition [35, 10]. These large volume changes are used in many artificial devices and are thought to play an important role in certain physiological systems [35, 7, 28]. The study gel swelling, and more generally of gel dynamics, is thus important from both practical and theoretical standpoints.

In this paper, we shall focus on polyelectrolyte gels; the polymer network contains fixed charge groups that dissociate and deliver counterions into the solvent. Polyelectrolyte gels form an important class of gels studied experimentally and used in applications. Indeed, the volume phase transition is most easily realized in polyelectrolyte gels [11, 35]. Most biological gels are also of this type.

Many of the early theoretical studies on gels focused on the static equilibrium state. A pioneering study on the dynamics of gels is [38], in which the authors examine the dynamics of a neutral gel around an equilibrium swelled state. As such, this was a small deformation theory. Various extensions of this theory have been proposed by many authors [5, 43, 31, 8, 9, 22, 23]. The standard theory describes the gel as a two-phase medium where the gel is viewed as an elastic polymer network (phase 1) permeated by a viscous fluid (phase 2).

Statics of polyelectrolyte gels are studied in [30], which has since been extended in many directions [35]. The dynamics of polyelectrolyte gels has also received a great deal of attention, and systems of evolution equations have been proposed by many authors [14, 12, 15, 25, 27, 40, 39, 44, 26, 6, 1]. A standard approach, which we shall adopt in this dissertation, is to treat polyelectrolyte gels as a two phase medium of polymer network and fluid, with the ions being treated as solute species dissolved in the fluid. But even within this same approach, there are various disagreements among the different models proposed by different authors.

In this dissertation, I shall introduce a system of partial differential equations (PDEs) describing the dynamics of a polyelectrolyte gel immersed in fluid. What sets our model apart from those of previous work is that its formulation is guided by the requirement that the system, as a whole, must satisfy a free energy identity. We arrive at a physically consistent system of equations in the bulk of the gel and in the surrounding fluid. Considerations of free energy dissipation also allow us to propose a general class of interface conditions to be satisfied at the moving gel-fluid interface. On the other hand, we apply Onsager's variational principle to derive all dynamic equations and boundary conditions. We believe that this is a particularly important contribution of our model; indeed, in previous work, the treatment of boundary or interface conditions has been somewhat simplistic, if not an afterthought.

The dissertation is organized as follows. The first chapter deals with neutral gel without involving ion species. In section 2.1, we present the skeletal framework of our model. The gel is treated as a two-phase medium consisting of the polymer network phase and a fluid phase. We write down the mass and momentum balance equations as well as the interface conditions at the gel-fluid interface. The normal velocity of the gel surface is equal to the normal velocity of the polymer network. The fluid inside the gel may flow into or out of the gel. There are two interface conditions for momentum balance. One condition concerns the balance of the total stress across the interface, and the other concerns the balance of stress within the fluid phase. In this section, we do not specify the constitutive laws for the polymer network and fluid stresses or the body forces. We end the section by proving an energy identity that is valid regardless of specific constitutive laws.

In section 2.2, we propose a purely mechanical model of a neutral gel immersed in fluid. We specify the polymer stress as a sum of the Flory-Huggins stress and an elastic stress. We treat the fluid as a newtonian viscous fluid. We also introduce a frictional body force between the polymer network and fluid. We propose a novel class of boundary conditions at the gel-fluid interface. Some previously proposed boundary conditions can be seen as limiting cases of the general class we present here [5, 43, 31]. We then prove a free energy identity satisfied by this system. The inertial, elastic and mixing energies of the gel are dissipated through viscous and frictional forces. The proposed interface conditions result in boundary dissipation of the free energy.

In section 2.3, we apply Onsager's variational principle to our model. The Onsager's principle is a systematic way of deriving dynamic equations for soft condensed matter systems. First, we illustrate the method by analysing a simple mechanical example. For our model, we define the potential energy, clarify the kinematic relations and kinematic constraints, and show that the model follows from Onsager's variational principle: the fluid flow obeying the force balance equations and appropriate interface conditions minimizes the rate of energy dissipation. The dynamic equations and boundary conditions follow as a consequence and match with those in section 2.2.

In the last section 2.4, we analyse the exponential decay rates of one-dimensional nonionic gel near the equilibria. We consider the viscosity and friction effects, both in the gel and on the interface. The trend of eigenvalues of the linearized equations are depicted by key parameters such as friction coefficient, permeability and viscosity. As it will be seen later, the sequence of eigenvalues in the purely mechanical model can be treated as the intrinsic eigenvalues of the polymer, in the ionic system.

The next chapter deals with polyelectrolyte gels. In section 3.1, we discuss the inclusion of ionic electrodiffusion. Ions diffuse and flow down the electrostatic potential gradient in the fluid phase of the gel as well as in the surrounding fluid. The electrostatic potential satisfies the Poisson equation. We allow the dielectric constant within the gel to depend on the volume fraction of the polymer network. The mechanical stress and body forces set forth in Section 2.2 are now augmented by the electrical forces. We conclude the section by showing that this system too satisfies a free energy identity. In addition to the terms that were present in the purely mechanical model of Section 2.2, the free energy now consists of an electrostatic term as well as an entropic contribution from the ionic concentrations.

The Debye length is typically very small in polyelectrolyte gels, and thus the bulk of the gel as well as the surrounding fluid is nearly electroneutral. In section 3.2, we formulate the appropriate equations in this electroneutral limit. The electroneutral limit corresponds formally to letting the dielectric constant tend to 0. This leads to the formation of boundary layers at the gel-fluid interface. We perform a boundary layer analysis to deduce the appropriate interface conditions in the electroneutral limit. What we find is that the van't Hoff law for osmotic pressure arises naturally in this limit. Our calculation points to the incompatibility of using *both* the van't Hoff law of osmotic pressure and the Poisson equation at the same time. It is easily checked that the condition for steady state gives us the well-established Donnan condition, set forth in the context of polyelectrolyte gels in [30].

The Onsager's variational principle is applied to the polyelectrolyte model in section 3.3. Here, we assume the dielectric constant to be zero, and derive the same equations and boundary conditions as from section 3.2.

Section 3.4 is divided into three parts. First, we present the steady state solutions and show the uniqueness as long as the initial value is given. Secondly, we consider a simple situation when the outside solution is always well mixed. The smallest eigenvalue found in section 3, called the principal eigenvalue of the polymer phase (PEP), and the principal eigenvalues of ion species (PEI) play an important role in the estimation of the minimal decay rate. Specifically, we examine how it changes as the gel becomes charged from the neutral state. Lastly, we turn to a more sophisticated situation involving dynamics of the outside solution, and show that with certain assumptions, the minimal decay rate must exceed the slowest component of gel and ion species.

Numerical simulations are demonstrated in section 3.5, in which we show a typical example of one-dimensional two-ion system. A transient period of fast movement near the interface can be seen at the beginning, then the gel and ions quickly approach the steady state. The exponential decay rate matches with the computation result in section 3.4.

Finally, appendix I devotes to Onsager's variational principle for positive dielectric constant, and appendix II discusses the numerical scheme of the ionic model.

Chapter 2

Gels: a mechanical model

2.1 Mass, Momentum and Energy Balance

We consider a gel that is in contact with its own fluid. We model the gel as an immiscible, incompressible mixture of two components, polymer network and solvent. The gel and the fluid occupy a smooth bounded region $\mathbb{U} \subset \mathbb{R}^3$. Let $\Omega_t \subset \mathbb{U}$ be the region where the gel is present at time t. We assume that $\Gamma_t \equiv \partial\Omega_t, \Gamma_t \cap \partial\mathbb{U} = \emptyset$. This means that the gel is completely immersed in the fluid. We denote the fluid region by $\mathcal{R}_t \equiv \mathbb{U}\backslash(\Omega_t \cup \Gamma_t)$.

At each point in Ω_t, define the volume fractions of the polymer component ϕ_1 and that of the solvent component ϕ_2. Assuming that there are neither voids nor additional volume-occupying components in the system, we have:

$$\phi_1 + \phi_2 = 1 \tag{2.1}$$

for any point inside Ω_t. Let $\mathbf{v}_i, i = 1, 2$ be the velocities of the polymer and solvent components respectively. The volume fractions ϕ_1 and ϕ_2 satisfy the volume transport equations:

$$\frac{\partial \phi_i}{\partial t} + \nabla \cdot (\mathbf{v}_i \phi_i) = 0,\ i = 1, 2. \tag{2.2}$$

The above and (2.1) implies the following incompressibility condition for the gel:

$$\nabla \cdot (\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) = 0. \tag{2.3}$$

Let $\gamma_i, i = 1, 2$ be the intrinsic mass densities of the polymer and solvent components respectively. The mass density of each component is, then, given by $\gamma_i\phi_i, i = 1, 2$. We assume that $\gamma_i, i = 1, 2$ are positive constants. Multiplying (2.2) by γ_i, (2.2) may also be seen as a statement of mass balance.

Linear momentum balance is given as follows:

$$\gamma_i\phi_i\left(\frac{\partial \mathbf{v}_i}{\partial t} + \mathbf{v}_i \cdot \nabla \mathbf{v}_i\right) = \nabla \cdot \mathcal{T}_i - \phi_i \nabla p_i + \mathbf{f}_i + \mathbf{g}_i,\ i = 1, 2 \tag{2.4}$$

where $\mathcal{T}_i$ and p_i are the stress tensors and pressures in the polymer and solvent components. The term $\mathbf{f}_i + \mathbf{g}_i$ is the body force, which we divide into two parts for reasons that will become clear below. In most cases of practical interest, inertial terms can be safely neglected, and we may thus formally set $\gamma_i = 0$. We nonetheless retain the inertial terms for theoretical completeness. We henceforth let:

$$p_1 = p + p_\Delta,\ p_2 = p. \tag{2.5}$$

We shall refer to $p_2 = p$ as the pressure and to p_Δ as the pressure difference. The pressure p is determined by the incompressibility constraint. We require that p_Δ and $\mathbf{f}_i$ satisfy the following condition. There exists a tensor $\mathcal{S}_g$ such that:

$$\nabla \cdot \mathcal{S}_g = -\phi_1 \nabla p_\Delta + \mathbf{f}_1 + \mathbf{f}_2. \tag{2.6}$$

The significance of this condition can be seen as follows. If we take the sum of equation (2.4) in i and use (2.6), we have:

$$\sum_{i=1}^{2} \gamma_i\phi_i\left(\frac{\partial \mathbf{v}_i}{\partial t} + \mathbf{v}_i \cdot \nabla \mathbf{v}_i\right) = \nabla \cdot (\mathcal{T}_1 + \mathcal{T}_2 + \mathcal{S}_g - pI) + \mathbf{g}_1 + \mathbf{g}_2, \tag{2.7}$$

where I is the 3×3 identity matrix. Condition (2.6) thus ensures that the total force acting on the gel at each point can be written as the divergence of a tensor except for the body forces $\mathbf{g}_i$. This is equivalent to saying that we have local momentum conservation in the absence of the body forces $\mathbf{g}_i$.

We assume $\mathcal{R}_t$ is filled with an incompressible fluid. Let $\mathbf{v}_\mathrm{f}$ be the velocity field of the fluid in $\mathcal{R}_t$.

$$\gamma_2\left(\frac{\partial \mathbf{v}_\mathrm{f}}{\partial t} + \mathbf{v}_\mathrm{f} \cdot \nabla \mathbf{v}_\mathrm{f}\right) = \nabla \cdot \mathcal{T}_\mathrm{f} - \nabla p + \mathbf{f}_\mathrm{f}, \tag{2.8}$$

$$\nabla \cdot \mathbf{v}_{\mathrm{f}} = 0, \tag{2.9}$$

where $\mathcal{T}_{\mathrm{f}}$ is the stress tensor, p is the pressure and $\mathbf{f}_{\mathrm{f}}$ is the body force. We require, as in (2.6), that $\mathbf{f}_{\mathrm{f}}$ can be written as the divergence of a tensor:

$$\nabla \cdot \mathcal{S}_{\mathrm{f}} = \mathbf{f}_{\mathrm{f}}. \tag{2.10}$$

In this paper, we do not consider extra body forces in $\mathcal{R}_t$ that cannot be written as divergence of a tensor.

We must specify the constitutive relations for the stress tensors $\mathcal{T}_i, \mathcal{T}_{\mathrm{f}}$, the body forces $\mathbf{f}_i, \mathbf{g}_i, \mathbf{f}_{\mathrm{f}}$ and the pressure difference p_Δ. We relegate this discussion to later sections since the calculations in this section do not depend on the specific form of the stresses or the body forces. Suffice it to say, at this point, that the fluid will be treated as viscous and the polymer phase as predominantly elastic. The body force may include a friction term and an electrostatic term.

We now turn to boundary conditions. First of all, notice that Ω_t is the region where the gel is present, and thus, Γ_t must move with the velocity of the polymer component. Let $\mathbf{n}$ be the unit normal vector on Γ_t pointing outward from Ω_t into $\mathcal{R}_t$. Let v_Γ be the normal velocity of Γ_t where we take the outward direction to be positive. We have:

$$\mathbf{v}_1 \cdot \mathbf{n} = v_\Gamma \text{ on } \Gamma_t. \tag{2.11}$$

By conservation of mass of the fluid phase, we must have:

$$(\mathbf{v}_{\mathrm{f}} - \mathbf{v_1}) \cdot \mathbf{n} = \phi_2(\mathbf{v}_2 - \mathbf{v}_1) \cdot \mathbf{n} \equiv w \tag{2.12}$$

We name the above quantity w. Let us postulate that the water velocity tangential to the surface Γ is equal on both sides of Γ:

$$(\mathbf{v}_{\mathrm{f}} - \mathbf{v}_1)_\parallel = (\mathbf{v}_2 - \mathbf{v}_1)_\parallel \equiv \mathbf{q} \tag{2.13}$$

where we have named the above quantity $\mathbf{q}$. Note that $\mathbf{q}$ is a vector that is tangent to the membrane.

We next consider force balance across the interface Γ. Consider a point on $\mathbf{x} \in \Gamma$ at a particular time t, and let us observe this point in an inertial frame traveling with the same velocity as the polymer at point $\mathbf{x}$ at time t. Given (2.12) and (2.13), we will observe water in the fluid region traveling at velocity $w\mathbf{n}+\mathbf{q}$ and water in the gel region traveling with velocity $w/\phi_2\mathbf{n}+\mathbf{q}$. The mass of water passing from the gel region to the water region per unit time at point $\mathbf{x}$ at time t is given by $\gamma_2 w$. As water comes out of the gel region into the water region, there is the following amount of momentum gain per unit time:

$$\gamma_2 w\left((w\mathbf{n}+\mathbf{q})-\left(\frac{w}{\phi_2}\mathbf{n}+\mathbf{q}\right)\right). \tag{2.14}$$

On the other hand, the force acting at the interface is given by:

$$(\mathcal{T}_{\mathrm{f}}+\mathcal{S}_{\mathrm{f}})\mathbf{n}-(\mathcal{T}_1+\mathcal{T}_2+\mathcal{S}_g)\mathbf{n}+[p]\mathbf{n},\ [p]=p|_{\Omega_t}-p|_{\mathcal{R}_t} \tag{2.15}$$

where $\cdot|_{\Omega_t}$ and $\cdot|_{\mathcal{R}_t}$ shall henceforth denote evaluation on the Ω_t side and the $\mathcal{R}_t$ side of Γ_t respectively. We shall also use the notation $[\cdot]\equiv\cdot|_{\Omega_t}-\cdot|_{\mathcal{R}_t}$ to denote the jump in the enclosed quantity across Γ_t. The two quantities, (2.14) and (2.15) must balance, which leads to the boundary condition:

$$(\mathcal{T}_{\mathrm{f}}+\mathcal{S}_{\mathrm{f}})\mathbf{n}-(\mathcal{T}_1+\mathcal{T}_2+\mathcal{S}_g)\mathbf{n}+[p]\mathbf{n}=\gamma_2 w^2\left(1-\frac{1}{\phi_2}\right)\mathbf{n}. \tag{2.16}$$

Note that the difference in the stress across the boundary is normal to the membrane. In particular, we have:

$$((\mathcal{T}_{\mathrm{f}}+\mathcal{S}_{\mathrm{f}})\mathbf{n}-(\mathcal{T}_1+\mathcal{T}_2+\mathcal{S}_g)\mathbf{n})\cdot\mathbf{q}=0 \tag{2.17}$$

since $\mathbf{q}$ is tangential to the surface Γ.

On the outer surface $\partial\mathbb{U}$, we let:

$$\mathbf{v}_{\mathrm{f}}=0. \tag{2.18}$$

At this point, we have the boundary conditions (2.13), (2.12) and (2.16) on Γ, which together give us six boundary conditions. Mass balance and total force balance would provide the necessary number of boundary conditions if the interior of Ω_t were composed of a one-phase medium. Here, the interior of Ω_t is a two-phase gel. We thus require additional boundary conditions. This will be discussed in subsequent sections.

We now turn to mass, linear momentum and energy balance. Before going further, we make note of two useful identities. Given a smooth function Q defined in Ω_t, we have:

$$\frac{d}{dt}\int_{\Omega_t} Q d\mathbf{x} = \int_{\Omega_t} \frac{\partial Q}{\partial t} d\mathbf{x} + \int_{\Gamma_t} Q v_\Gamma dS = \int_{\Omega_t} \frac{\partial Q}{\partial t} d\mathbf{x} + \int_{\Gamma_t} Q \mathbf{v}_1 \cdot \mathbf{n} dS \tag{2.19}$$

where dS denotes integration over the surface Γ_t. We used (2.11) in the second equality. The reader will recognize that this is nothing other than the Reynolds transport theorem. Likewise, for a quantity Q defined in $\mathcal{R}_t$, we have:

$$\frac{d}{dt}\int_{\mathcal{R}_t} Q d\mathbf{x} = \int_{\mathcal{R}_t} \frac{\partial Q}{\partial t} d\mathbf{x} - \int_{\Gamma_t} Q \mathbf{v}_1 \cdot \mathbf{n} dS. \tag{2.20}$$

Since the use of the above two identities will be frequent, we shall not cite their use in what follows.

Let us now check that the boundary conditions (2.12), (2.13) and (2.16) indeed lead to mass and momentum conservation.

We first check that the amount of fluid is conserved:

$$\begin{aligned}
&\frac{d}{dt}\left(\int_{\Omega_t} \phi_2 d\mathbf{x} + \int_{\mathcal{R}_t} d\mathbf{x}\right) \\
=&\int_{\Gamma_t} \phi_2(\mathbf{v}_2 - \mathbf{v}_1)\cdot\mathbf{n} dS - \int_{\Gamma_t} (\mathbf{v}_\mathrm{f} - \mathbf{v}_1)\cdot\mathbf{n} dS + \int_{\partial\mathbb{U}} \mathbf{v}_\mathrm{f}\cdot\mathbf{n} dS \\
=&0,
\end{aligned} \tag{2.21}$$

where we used (2.12) and (2.18) in the second equality.

Let us consider linear momentum conservation.

$$
\begin{aligned}
&\frac{d}{dt}\left(\int_{\Omega_t}(\gamma_1\phi_1\mathbf{v}_1+\gamma_2\phi_2\mathbf{v}_2)\,d\mathbf{x}+\int_{\mathcal{R}_t}\gamma_2\mathbf{v}_\mathrm{f}d\mathbf{x}\right)\\
=&\int_{\Gamma_t}(\gamma_2\phi_2\mathbf{v}_2(\mathbf{v}_1-\mathbf{v}_2)\cdot\mathbf{n}+(\mathcal{T}_1+\mathcal{T}_2+\mathcal{S}_g)\mathbf{n}-p\mathbf{n})\,dS\\
&-\int_{\Gamma_t}(\gamma_2\mathbf{v}_\mathrm{f}(\mathbf{v}_1-\mathbf{v}_\mathrm{f})\cdot\mathbf{n}+(\mathcal{T}_\mathrm{f}+\mathcal{S}_\mathrm{f})\mathbf{n}-p\mathbf{n})\,dS\\
&+\int_{\partial\mathbb{U}}((\mathcal{T}_\mathrm{f}+\mathcal{S}_\mathrm{f})\mathbf{n}-p\mathbf{n})dS+\int_{\Omega_t}(\mathbf{g}_1+\mathbf{g}_2)\,d\mathbf{x}+\int_{\mathcal{R}_t}\mathbf{f}_\mathrm{f}d\mathbf{x}\\
=&\int_{\Gamma_t}\left(\gamma_2\left(1-\frac{1}{\phi_2}\right)w^2+((\mathcal{T}_1+\mathcal{T}_2+\mathcal{S}_g)\mathbf{n}-(\mathcal{T}_\mathrm{f}+\mathcal{S}_\mathrm{f})\mathbf{n}-[p]\mathbf{n}\right)dS\\
&+\int_{\partial\mathbb{U}}((\mathcal{T}_\mathrm{f}+\mathcal{S}_\mathrm{f})\mathbf{n}-p\mathbf{n})\,dS+\int_{\Omega_t}(\mathbf{g}_1+\mathbf{g}_2)\,d\mathbf{x}\\
=&\int_{\partial\mathbb{U}}((\mathcal{T}_\mathrm{f}+\mathcal{S}_\mathrm{f})\mathbf{n}-p\mathbf{n})\,dS+\int_{\Omega_t}(\mathbf{g}_1+\mathbf{g}_2)\,d\mathbf{x}
\end{aligned}
\tag{2.22}
$$

where $\mathbf{n}$ on $\partial\mathbb{U}$ is the outward unit normal on $\partial\mathbb{U}$. We used (2.6) and (2.10) in the first equality, (2.12) in the second and third equalities, (2.13) in the third equality and (2.16) in the last equality. Change in total linear momentum is thus due only to body forces $\mathbf{g}_i$ and forces on the outer boundary. The following result is now immediate.

Lemma 2.1. *Suppose $\phi_i, \mathbf{v}_i, \mathbf{v}_\mathrm{f}$ are smooth functions that satisfy* (2.1), (2.2), (2.4), (2.8), (2.9), (2.12), (2.13), (2.16), (2.18) *and suppose $p_\Delta, \mathbf{f}_i, \mathbf{f}_\mathrm{f}$ satisfy* (2.6) *and* (2.10). *Suppose in addition that*

$$\mathbf{g}_1+\mathbf{g}_2=0. \tag{2.23}$$

Then, we have total linear momentum conservation in the following sense:

$$\frac{d}{dt}\left(\int_{\Omega_t}(\gamma_1\phi_1\mathbf{v}_1+\gamma_2\phi_2\mathbf{v}_2)\,d\mathbf{x}+\int_{\mathcal{R}_t}\gamma_2\mathbf{v}_\mathrm{f}d\mathbf{x}\right)=\int_{\partial\mathbb{U}}((\mathcal{T}_\mathrm{f}+\mathcal{S}_\mathrm{f})\mathbf{n}-p\mathbf{n})\,dS. \tag{2.24}$$

The question of energy balance will be stated later once the constitutive laws have been specified. Here we state a preliminary result that does not depend on the form of the constitutive laws. We shall find this result useful in subsequence sections.

Lemma 2.2. *Suppose $\phi_i, \mathbf{v}_i, \mathbf{v}_\mathrm{f}$ are smooth functions that satisfy* (2.1), (2.2), (2.4), (2.8), (2.9), (2.12), (2.13), (2.16), (2.18) *and suppose $p_\Delta, \mathbf{f}_i, \mathbf{f}_\mathrm{f}$ satisfy* (2.6) *and*

(2.10). *We have:*

$$\begin{aligned}
&\frac{d}{dt}\left(\int_{\Omega_t}\left(\frac{1}{2}\gamma_1\phi_1\left|\mathbf{v}_1\right|^2+\frac{1}{2}\gamma_2\phi_2\left|\mathbf{v}_2\right|^2\right)d\mathbf{x}+\int_{\mathcal{R}_t}\frac{1}{2}\gamma_2\left|\mathbf{v}_\mathrm{f}\right|^2d\mathbf{x}\right)\\
=&-\int_{\Omega_t}\left((\nabla\mathbf{v}_1):\mathcal{T}_1+(\nabla\mathbf{v}_2):\mathcal{T}_2\right)d\mathbf{x}-\int_{\Omega_\mathrm{f}}(\nabla\mathbf{v}_\mathrm{f}):\mathcal{T}_\mathrm{f}d\mathbf{x}\\
&+\int_{\Omega_t}\left((-\phi_1\nabla p_\Delta+\mathbf{f}_1+\mathbf{g}_1)\cdot\mathbf{v}_1+(\mathbf{f}_2+\mathbf{g}_2)\cdot\mathbf{v}_2\right)d\mathbf{x}+\int_{\mathcal{R}_t}\mathbf{f}_\mathrm{f}\cdot\mathbf{v}_\mathrm{f}d\mathbf{x}\\
&-\int_\Gamma\left(((\mathcal{S}_g-\mathcal{S}_\mathrm{f})\mathbf{n})\cdot\mathbf{v}_1+w\Pi_\perp+\mathbf{q}\cdot\Pi_\parallel\right)dS,
\end{aligned}\tag{2.25}$$

where $\Pi_\parallel\equiv(\mathcal{T}_1\mathbf{n})_\parallel$ *is the component of* $\mathcal{T}_1\mathbf{n}$ *parallel to the boundary and*

$$\Pi_\perp=\left(\mathbf{n}\cdot(\mathcal{T}_\mathrm{f}\mathbf{n})-\frac{1}{2}\gamma_2w^2\right)-\left(\mathbf{n}\cdot\left(\frac{\mathcal{T}_2}{\phi_2}\right)\mathbf{n}-\frac{1}{2}\gamma_2\left(\frac{w}{\phi_2}\right)^2\right)+[p].\tag{2.26}$$

Proof. Let us compute the left hand side of (2.25):

$$\begin{aligned}
&\frac{d}{dt}\left(\int_{\Omega_t}\left(\frac{1}{2}\gamma_1\phi_1\left|\mathbf{v}_1\right|^2+\frac{1}{2}\gamma_2\phi_2\left|\mathbf{v}_2\right|^2\right)d\mathbf{x}+\int_{\Omega_\mathrm{f}}\frac{1}{2}\gamma_2\left|\mathbf{v}_\mathrm{f}\right|^2d\mathbf{x}\right)\\
=&\int_{\Omega_t}\left(\mathbf{v}_1(\nabla\cdot\mathcal{T}_1)+\mathbf{v}_2(\nabla\cdot\mathcal{T}_2)\right)d\mathbf{x}+\int_{\Omega_\mathrm{f}}\mathbf{v}_\mathrm{f}(\nabla\cdot\mathcal{T}_\mathrm{f})d\mathbf{x}\\
&+\int_{\Omega_t}\left((-\phi_1\nabla p_\Delta+\mathbf{f}_1+\mathbf{g}_1)\cdot\mathbf{v}_1+(\mathbf{f}_2+\mathbf{g}_2)\cdot\mathbf{v}_2\right)d\mathbf{x}\\
&-\int_{\Omega_t}(\phi_1\mathbf{v}_1+\phi_2\mathbf{v}_2)\cdot\nabla p d\mathbf{x}-\int_{\mathcal{R}_t}\mathbf{v}_\mathrm{f}\cdot\nabla p d\mathbf{x}\\
&+\int_{\Gamma_t}\left(\frac{1}{2}\gamma_2\phi_2\left|\mathbf{v}_2\right|^2(\mathbf{v}_1-\mathbf{v}_2)\cdot\mathbf{n}-\frac{1}{2}\gamma_2\left|\mathbf{v}_\mathrm{f}\right|^2(\mathbf{v}_1-\mathbf{v}_\mathrm{f})\cdot\mathbf{n}\right)dS\\
=&-\int_{\Omega_t}\left((\nabla\mathbf{v}_1):\mathcal{T}_1+(\nabla\mathbf{v}_2):\mathcal{T}_2\right)d\mathbf{x}-\int_{\mathcal{R}_t}(\nabla\mathbf{v}_\mathrm{f}):\mathcal{T}_\mathrm{f}d\mathbf{x}\\
&+\int_{\Omega_t}\left((-\phi_1\nabla p_\Delta+\mathbf{f}_1+\mathbf{g}_1)\cdot\mathbf{v}_1+(\mathbf{f}_2+\mathbf{g}_2)\cdot\mathbf{v}_2\right)d\mathbf{x}\\
&+\int_{\Gamma_t}\left((\mathcal{T}_1\mathbf{n}-\phi_1p\mathbf{n})\cdot\mathbf{v}_1+(\mathcal{T}_2\mathbf{n}-\phi_2p\mathbf{n})\cdot\mathbf{v}_2-(\mathcal{T}_\mathrm{f}\mathbf{n}-p\mathbf{n})\cdot\mathbf{v}_\mathrm{f}\right)dS\\
&+\int_{\Gamma_t}\left(\frac{1}{2}\gamma_2\phi_2\left|\mathbf{v}_2\right|^2(\mathbf{v}_1-\mathbf{v}_2)\cdot\mathbf{n}-\frac{1}{2}\gamma_2\left|\mathbf{v}_\mathrm{f}\right|^2(\mathbf{v}_1-\mathbf{v}_\mathrm{f})\cdot\mathbf{n}\right)dS.
\end{aligned}\tag{2.27}$$

where we used (2.3) and (2.9) in the second equality. Let us evaluate the last two boundary integrals. Using (2.12), (2.13) and (2.16), (2.17) we have:

$$
\begin{aligned}
&(\mathcal{T}_1\mathbf{n} - \phi_1 p\mathbf{n}) \cdot \mathbf{v}_1 + (\mathcal{T}_2\mathbf{n} - \phi_2 p\mathbf{n}) \cdot \mathbf{v}_2 - (\mathcal{T}_\mathrm{f}\mathbf{n} - p\mathbf{n}) \cdot \mathbf{v}_\mathrm{f} \\
=&((\mathcal{T}_1 + \mathcal{T}_2)\mathbf{n} - \mathcal{T}_\mathrm{f}\mathbf{n} - [p]\mathbf{n}) \cdot \mathbf{v}_1 \\
&+ \left(\mathbf{n} \cdot \left(\frac{\mathcal{T}_2}{\phi_2}\mathbf{n}\right) - \mathbf{n} \cdot (\mathcal{T}_\mathrm{f}\mathbf{n}) - [p]\right) w + (\mathcal{T}_2\mathbf{n} - \mathcal{T}_\mathrm{f}\mathbf{n}) \cdot \mathbf{q} \\
=&-((\mathcal{S}_g - \mathcal{S}_g)\mathbf{n}) \cdot \mathbf{v}_1 - \gamma_2 w^2 \left(1 - \frac{1}{\phi_2}\right)(\mathbf{v}_1 \cdot \mathbf{n}) \\
&+ \left(\mathbf{n} \cdot \left(\frac{\mathcal{T}_2}{\phi_2}\mathbf{n}\right) - \mathbf{n} \cdot (\mathcal{T}_\mathrm{f}\mathbf{n}) - [p]\right) w - (\mathcal{T}_1\mathbf{n}) \cdot \mathbf{q}
\end{aligned} \tag{2.28}
$$

On the other hand,

$$
\begin{aligned}
&\frac{1}{2}\gamma_2\phi_2 |\mathbf{v}_2|^2 (\mathbf{v}_1 - \mathbf{v}_2) \cdot \mathbf{n} - \frac{1}{2}\gamma_2 |\mathbf{v}_\mathrm{f}|^2 (\mathbf{v}_1 - \mathbf{v}_\mathrm{f}) \cdot \mathbf{n} \\
=&-\frac{1}{2}\gamma_2 \left|\mathbf{v}_1 + \frac{w}{\phi_2}\mathbf{n} + \mathbf{q}\right|^2 w + \frac{1}{2}\gamma_2 |\mathbf{v}_1 + w\mathbf{n} + \mathbf{q}|^2 w \\
=&\gamma_2 w^2 \left(1 - \frac{1}{\phi_2}\right)(\mathbf{v}_1 \cdot \mathbf{n}) - \left(\frac{1}{2}\gamma_2 \left(\frac{w}{\phi_2}\right)^2 - \frac{1}{2}\gamma_2 w^2\right) w
\end{aligned} \tag{2.29}
$$

where we used (2.12) in the first equality. Combining (2.27), (2.28) and (2.29), we obtain (2.25). □

2.2 A Mechanical Model

We now consider a mechanical model of the gel immersed in fluid. To describe the elasticity of the polymer component, we consider the following. Let $\Omega \in \mathbb{R}^3$ be the reference domain of the polymer network, with coordinates $\mathbf{X}$. A point $\mathbf{X} \in \Omega$ is mapped to a point $\mathbf{x} \in \Omega_t$ by the smooth deformation map $\boldsymbol{\varphi}_t$:

$$\mathbf{x} = \boldsymbol{\varphi}_t(\mathbf{X}). \tag{2.30}$$

Henceforth, the small case $\mathbf{x}$ denotes position in Ω_t and the large case $\mathbf{X}$ denotes position in the reference domain Ω. Note that the velocity of the polymer phase $\mathbf{v}_1$ and $\boldsymbol{\varphi}_t$ are related through:

$$\mathbf{v}_1(\boldsymbol{\varphi}_t(\mathbf{X}), t) = \frac{\partial}{\partial t}(\boldsymbol{\varphi}_t(\mathbf{X})). \tag{2.31}$$

We shall let $F = \nabla_{\mathbf{X}}\boldsymbol{\varphi}_t$ be the deformation gradient, where $\nabla_{\mathbf{X}}$ denotes the gradient with respect to the reference coordinate. Define $\mathcal{F} = F \circ \boldsymbol{\varphi}_t^{-1}$ so that $\mathcal{F}$ is the deformation gradient evaluated in Ω_t rather than in Ω. It is a direct consequence of (2.31) that F satisfies the following transport equation:

$$\left.\frac{\partial F}{\partial t}\right|_{\mathbf{X}=\boldsymbol{\varphi}_t^{-1}(\mathbf{x})} = \frac{\partial \mathcal{F}}{\partial t} + (\mathbf{v}_1 \cdot \nabla)\mathcal{F} = (\nabla \mathbf{v}_1)\mathcal{F}. \tag{2.32}$$

Using the deformation gradient, condition (2.2) for $i = 1$ can be expressed as:

$$(\phi_1 \circ \boldsymbol{\varphi}_t)\mathrm{det}F = \phi_I \tag{2.33}$$

where ϕ_I is a function defined on Ω that takes values between 0 and 1. This should be clear from the meaning of the deformation gradient, but can also be checked directly using (2.32) and (2.2). The function ϕ_I is the volume fraction of the polymer component in the reference configuration.

We suppose that the stress of the gel is given by the following:

$$\begin{aligned} \mathcal{T}_1 &= \mathcal{T}_1^{\mathrm{visc}} + \mathcal{T}_1^{\mathrm{elas}}, \\ \mathcal{T}_1^{\mathrm{visc}} &= \eta_1(\nabla \mathbf{v}_1 + (\nabla \mathbf{v}_1)^T), \quad \mathcal{T}_1^{\mathrm{elas}} = \phi_1 \frac{\partial \mathcal{W}_{\mathrm{elas}}(\mathcal{F})}{\partial \mathcal{F}} \mathcal{F}^T. \end{aligned} \tag{2.34}$$

The viscosity $\eta_1 > 0$ may be a function of ϕ_1, in which case we assume this function is smooth and bounded. The function $\phi_1 \mathcal{W}_{\mathrm{elas}}$ is the elastic energy per unit volume. An example form of $\mathcal{W}_{\mathrm{elas}}$ is given by [31]:

$$\mathcal{W}_{\mathrm{elas}} = \mu_E \left(\frac{1}{2p}\left(\|F\|^{2p} - \|I\|^{2p} \right) + \frac{\|I\|^{2(p-1)}}{\beta}\left((\mathrm{det}F)^{-\beta} - 1 \right) \right), \; p \geq 1, \tag{2.35}$$

where $\|\cdot\|$ is the Frobenius norm of the matrix and I is the 3×3 identity matrix, μ_E is the elastic modulus, and β is a modulus related to polymer compressibility. The above reduces to compressible neo-Hookean elasticity if we set $p = 1$.

The pressure difference p_Δ is given as follows:

$$p_\Delta = \frac{d\mathcal{W}_{\mathrm{FH}}}{d\phi_1}, \quad \mathcal{W}_{\mathrm{FH}} = \frac{k_B T}{v_s}\left(\frac{v_s}{v_p}\phi_1 \ln \phi_1 + \phi_2 \ln \phi_2 + \chi \phi_1 \phi_2 \right). \tag{2.36}$$

The function $\mathcal{W}_{\mathrm{FH}}$ is the Flory-Huggins mixing energy where $k_B T$ is the Boltzmann constant times absolute temperature, v_p and v_s are the volume occupied by a single molecule of polymer and solvent respectively and χ is a parameter that describes the interaction energy between the polymer and solvent. Since $v_s \ll v_p$ for a crosslinked polymer network, the first term in $\mathcal{W}_{\mathrm{FH}}$ is often taken to be 0. By substituting $\phi_2 = 1 - \phi_1$ from (2.1), we may view $\mathcal{W}_{\mathrm{FH}}$ as a function only of ϕ_1. Note that the above prescription of the pressure difference p_Δ is symmetric with respect to the role played by the polymer and solvent components in the following sense:

$$p_\Delta = p_1 - p_2 = \frac{d\mathcal{W}_{\mathrm{FH}}}{d\phi_1} = -\frac{d\mathcal{W}_{\mathrm{FH}}}{d\phi_2} = -(p_2 - p_1), \tag{2.37}$$

where we used (2.5) and $d\mathcal{W}_{\mathrm{FH}}/d\phi_2$ above refers to the derivative of $\mathcal{W}_{\mathrm{FH}}$ when viewed as a function of ϕ_2 only.

We let:

$$\mathbf{f}_1 = \mathbf{f}_2 = 0. \tag{2.38}$$

If we set

$$\mathcal{S}_g = \mathcal{S}_g^{\mathrm{FH}} \equiv \left(\mathcal{W}_{\mathrm{FH}}(\phi_1) - \phi_1 \frac{d}{d\phi_1}\mathcal{W}_{\mathrm{FH}}(\phi_1)\right) I, \tag{2.39}$$

we find that (2.6) is satisfied.

We point out that there is some arbitrariness in what we call the pressure difference and what we call the stress. Indeed we may prescribe $\mathcal{T}_1$ and p_Δ as follows to obtain exactly the same equations as is obtained when using (2.34) and (2.36):

$$\mathcal{T}_1 = \mathcal{T}_1^{\mathrm{visc}} + \mathcal{T}_1^{\mathrm{elas}} + \mathcal{S}_g^{\mathrm{FH}}, \; p_\Delta = 0 \tag{2.40}$$

where I is the 3×3 identity matrix. Though mathematically equivalent, we find (2.34) and (2.36) more physically appealing since the polymer and solvent phases are treated symmetrically as far as the Flory-Huggins energy is concerned. Prescription (2.40) gives the impression that the Flory-Huggins energy "belongs" solely to the polymer network.

The body forces $\mathbf{g}_i$ are given by:

$$\mathbf{g}_1 = \mathbf{g}_{\mathrm{fric}} = -\kappa(\mathbf{v}_1 - \mathbf{v}_2), \; \mathbf{g}_2 = -\mathbf{g}_{\mathrm{fric}}. \tag{2.41}$$

Here, $\kappa > 0$ is the friction coefficient and may depend on ϕ_1.

We assume that the fluid is viscous:

$$\mathcal{T}_{2,\mathrm{f}} = \eta_{2,\mathrm{f}} \left(\nabla \mathbf{v}_{2,\mathrm{f}} + (\nabla \mathbf{v}_{2,\mathrm{f}})^T \right). \tag{2.42}$$

The viscosity $\eta_{\mathrm{f}} > 0$ is a constant and $\eta_2 > 0$ may be a (smooth and bounded) function of ϕ_2 (or equivalently, ϕ_1). For the body force, in the fluid, we let:

$$\mathbf{f}_{\mathrm{f}} = 0, \ \mathcal{S}_{\mathrm{f}} = 0. \tag{2.43}$$

Condition (2.10) is trivially satisfied with the above definitions of $\mathbf{f}_{\mathrm{f}}$ and $\mathcal{S}_{\mathrm{f}}$.

We now turn to boundary conditions. As was mentioned in the previous section, (2.12), (2.13) and (2.16) provide only six boundary conditions. We need three boundary conditions for each of the components in contact with the interface Γ_t. We have three components, the polymer and solvent components of the gel and the surrounding fluid. We thus need nine boundary conditions. We now specify the remaining three boundary conditions. They are:

$$\eta_{\perp} w = \Pi_{\perp}, \tag{2.44}$$

$$\eta_{\parallel} \mathbf{q} = \Pi_{\parallel} \equiv (\mathcal{T}_1 \mathbf{n})_{\parallel}, \tag{2.45}$$

where $\Pi_{\perp}$ was defined in (2.26) and $\eta_{\perp}$ and $\eta_{\parallel}$ are positive constants.

Condition (2.45) is a Navier-type slip boundary condition. If $\eta_{\parallel} \to \infty$, this amounts to taking $\mathbf{q} = 0$. This will give us a tangential no-slip boundary condition for the fluid.

Let us turn to condition (2.44). Note that $\Pi_{\perp}$ can be written as:

$$\begin{aligned} \Pi_{\perp} = \Pi_{\Omega_t} - \Pi_{\mathcal{R}_t}, \ \Pi_{\Omega_t} &= \frac{1}{2}\gamma_2 \left(\frac{w}{\phi_2} \right)^2 + p|_{\Omega_t} - \mathbf{n} \cdot \left(\frac{\mathcal{T}_2}{\phi_2} \right) \mathbf{n}, \\ \Pi_{\mathcal{R}_t} &= \frac{1}{2}\gamma_2 w^2 + p|_{\mathcal{R}_t} - \mathbf{n} \cdot (\mathcal{T}_{\mathrm{f}} \mathbf{n}). \end{aligned} \tag{2.46}$$

The quantities Π_{Ω_t} and $\Pi_{\mathcal{R}_t}$ can be seen as the energy per unit volume of fluid inside and outside the gel respectively. If we set $\eta_{\perp} = 0$, this is nothing other than the Bernoulli law for inviscid fluids. If $\eta_{\perp} > 0$, a friction force acts on the fluid as it passes the interface Γ_t. Boundary condition (2.44) has the peculiar feature that it is quadratic in w. This is problematic; given $\phi_2 < 1$ and the stress jump

$$\mathcal{T}_\Delta = [p] - \mathbf{n} \cdot \left(\frac{\mathcal{T}_2}{\phi_2}\right) \mathbf{n} + \mathbf{n} \cdot (\mathcal{T}_\mathrm{f} \mathbf{n}) \tag{2.47}$$

there can be two possible values of w. Note that this problem arises only if $\phi_2 < 1$, and is thus a difficulty that is unique to the situation in which a pure fluid is in contact with a two-component system. We expect condition (2.44) to be valid only for small values of w over which w is an increasing function of $\mathcal{T}_\Delta$ for fixed ϕ_2. This precludes the possibility of taking $\eta_\perp = 0$ if $\gamma_2 > 0$. We note that, for most, if not all situations of interest in gel modeling, the inertial terms can be safely neglected. This amounts to setting $\gamma_2 = 0$ (and $\gamma_1 = 0$) in which case this difficulty simply disappears. In the context of this Stokes approximation, it is perfectly reasonable to set $\eta_\perp = 0$. This is the fully permeable case. If we set $\eta_\perp \to \infty$, $w = 0$ and we have the fully impermeable case.

The following result states that the total free energy, given as the sum of the kinetic energy E_KE, the polymer elastic energy E_elas, the Flory-Huggins mixing energy E_FH, decreases through viscous or frictional dissipation in the bulk (I_visc) or on the interface (J_visc).

Theorem 2.1. *Let $\phi_i, \mathbf{v}_i$, and $\mathbf{v}_\mathrm{f}$, be smooth functions that satisfy* (2.1)*,* (2.2)*,* (2.4)*,* (2.8)*,* (2.9)*,* (2.12)*,* (2.13)*,* (2.16)*,* (2.18)*,* (2.44)*,* (2.45) *where the stress tensors, pressure difference and body forces are given by* (2.34)*,* (2.42)*,* (2.36)*,* (2.38)*,* (2.41) *and* (2.43)*. Then, we have total linear momentum conservation in the sense of Lemma* 2.1*. In addition, we have free energy dissipation in the following sense:*

$$\begin{aligned}
&\frac{d}{dt}\left(E_\mathrm{KE} + E_\mathrm{elas} + E_\mathrm{FH}\right) = -I_\mathrm{visc} - J_\mathrm{visc}, \\
&E_\mathrm{KE} = \int_{\Omega_t} \left(\frac{1}{2}\gamma_1\phi_1 \left|\mathbf{v}_1\right|^2 + \frac{1}{2}\gamma_2\phi_2\left|\mathbf{v}_2\right|^2\right) d\mathbf{x} + \int_{\mathcal{R}_t} \frac{1}{2}\gamma_2 \left|\mathbf{v}_\mathrm{f}\right|^2 d\mathbf{x}, \\
&E_\mathrm{elas} = \int_{\Omega_t} \phi_1 \mathcal{W}_\mathrm{elas}(\mathcal{F}) d\mathbf{x}, \quad E_\mathrm{FH} = \int_{\Omega_t} \mathcal{W}_\mathrm{FH}(\phi_1) d\mathbf{x}, \\
&I_\mathrm{visc} = \int_{\Omega_t} \left(\sum_{i=1}^{2} 2\eta_i \left\|\nabla_S \mathbf{v}_i\right\|^2 + \kappa\left|\mathbf{v}_1 - \mathbf{v}_2\right|^2\right) d\mathbf{x} + \int_{\mathcal{R}_t} 2\eta_\mathrm{f}\left\|\nabla_S \mathbf{v}_\mathrm{f}\right\|^2 d\mathbf{x}, \\
&J_\mathrm{visc} = \int_{\Gamma_t} \left(\eta_\perp w^2 + \eta_\parallel \left|\mathbf{q}\right|^2\right) dS,
\end{aligned} \tag{2.48}$$

where ∇_S is the symmetric part of the corresponding velocity gradient and $\|\cdot\|$ denotes *the Frobenius norm of the* 3×3 *matrix.*

Proof. Linear momentum balance is immediate from Lemma 2.1 since $\mathbf{g}_1 + \mathbf{g}_2$ by (2.41). We can prove this by a direct application of Lemma 2.2. Substitute (2.34), (2.42), (2.36), (2.38), (2.41), (2.43), (2.44) and (2.45) into (2.25). We see that (2.48) is immediate if we can show the following two identities:

$$\frac{d}{dt}\int_{\Omega_t} \phi_1 \mathcal{W}_{\text{elas}}(\mathcal{F}) d\mathbf{x} = \int_{\Omega_t} (\nabla \mathbf{v}_1) : \mathcal{T}_1^{\text{elas}} d\mathbf{x}, \tag{2.49}$$

$$\begin{aligned} \frac{d}{dt}\int_{\Omega_t} \mathcal{W}_{\text{FH}}(\phi_1) d\mathbf{x} = &\int_{\Gamma_t} ((\mathcal{S}_g - \mathcal{S}_{\text{f}})\mathbf{n}) \cdot \mathbf{v}_1 dS \\ &- \int_{\Omega_t} ((-\phi_1 \nabla p_\Delta + \mathbf{f}_1) \cdot \mathbf{v}_1 + \mathbf{f}_2 \cdot \mathbf{v}_2)\, d\mathbf{x}. \end{aligned} \tag{2.50}$$

First consider (2.49):

$$\begin{aligned} &\frac{d}{dt}\int_{\Omega_t} \phi_1 \mathcal{W}_{\text{elas}}(\mathcal{F}) d\mathbf{x} = \frac{d}{dt}\int_{\Omega} \phi_I \mathcal{W}_{\text{elas}}(F) d\mathbf{X} \\ &= \int_{\Omega} \phi_I \frac{\partial \mathcal{W}_{\text{elas}}(F)}{\partial F} : \frac{\partial F}{\partial t} d\mathbf{X} = \int_{\Omega_t} \phi_1 \frac{\partial \mathcal{W}_{\text{elas}}(\mathcal{F})}{\partial \mathcal{F}} : (\nabla \mathbf{v}_1 \mathcal{F})\, d\mathbf{x} \\ &= \int_{\Omega_t} \left(\phi_1 \frac{\partial \mathcal{W}_{\text{elas}}(\mathcal{F})}{\partial \mathcal{F}} \mathcal{F}^T \right) : (\nabla \mathbf{v}_1) d\mathbf{x} = \int_{\Omega_t} (\nabla \mathbf{v}_1) : \mathcal{T}_1^{\text{elas}} d\mathbf{x}, \end{aligned} \tag{2.51}$$

where we used (2.33) in the first and third equalities and (2.32) in the third equality. Let us now evaluate the right hand side of (2.50):

$$\begin{aligned} &\int_{\Gamma_t} (\mathcal{S}_g \mathbf{n}) \cdot \mathbf{v}_1 dS + \int_{\Omega_t} (\phi_1 \nabla p_\Delta) \cdot \mathbf{v}_1 d\mathbf{x} \\ &= \int_{\Gamma_t} \left(\mathcal{W}_{\text{FH}} - \phi_1 \frac{d\mathcal{W}_{\text{FH}}}{d\phi_1} \right) \mathbf{v}_1 \cdot \mathbf{n} dS + \int_{\Omega_t} \left(\phi_1 \mathbf{v}_1 \cdot \nabla \left(\frac{d\mathcal{W}_{\text{FH}}}{d\phi_1} \right) \right) d\mathbf{x} \\ &= \int_{\Gamma_t} (\mathcal{W}_{\text{FH}})\, \mathbf{v}_1 \cdot \mathbf{n} dS + \int_{\Omega_t} \left(\frac{d\mathcal{W}_{\text{FH}}}{d\phi_1} \frac{\partial \phi_1}{\partial t} \right) d\mathbf{x} = \frac{d}{dt}\int_{\Omega_t} \mathcal{W}_{\text{FH}} d\mathbf{x}, \end{aligned} \tag{2.52}$$

where we integrated by parts and used (2.2) in the second equality. □

2.3 Onsager's variational principle

Our goal in this section is to derive the equations for gel dynamics using Onsager's variational principle. Derivation using Onsager's variational principle has the advantage of being systematic and thus less prone to errors. It also has the attractive feature that the resulting equations automatically satisfy an energy identity (as we derived in section 2.2) as well as Onsager's reciprocity principle, which asserts the equality of cross-coefficients relating different thermodynamic forces.

To illustrate this general variational approach, we briefly consider the following simple example. Consider N masses $m_1, \cdots, m_N$, their positions $x_1, \cdots, x_N$ and velocities $v_1, \cdots, v_N$ which satisfy

$$m_i \frac{dv_i}{dt} = -\gamma_i v_i - \sum_{j \neq i} \gamma_{ij}(v_i - v_j) - kx_i \quad \text{for } i = 1, \cdots, N \tag{2.53}$$

in which γ_i, $\gamma_{ij} = \gamma_{ji} > 0$ are friction coefficients, $k > 0$ is the spring constant. Neglecting inertial terms, we have the force balance, or the *dynamic equations*:

$$\gamma_i v_i + \sum_{j \neq i} \gamma_{ij}(v_i - v_j) = -kx_i \quad \text{for } i = 1, \cdots, N \tag{2.54}$$

Note that x_i and v_i are linked through the *kinematic relation*:

$$\frac{dx_i}{dt} = v_i. \tag{2.55}$$

Let us multiply both sides of (2.54) with v_i and take the summation in i. With the help of (2.55), we obtain the following *energy relation*:

$$\frac{dU}{dt} = -2W,\ U = \sum_{i=1}^{N} \frac{1}{2} kx_i^2,\ 2W = \sum_{i=1}^{N} \gamma_i v_i^2 + \frac{1}{2} \sum_{i \neq j} \gamma_{ij}(v_i - v_j)^2. \tag{2.56}$$

The function U is the total potential energy of the system and W is called Rayleigh's dissipation function. Note that the dissipation is a quadratic function in the velocity.

We now reverse this process. Suppose we are given the kinematic relation (2.55) and the energy relation (2.56). Consider the expression:

$$R = \frac{dU}{dt} + W = \sum_{i=1}^{N} \frac{\partial U}{\partial x_i} \frac{dx_i}{dt} + W(v_1, \cdots, v_N) = \sum_{i=1}^{N} \frac{\partial U}{\partial x_i} v_i + W(v_1, \cdots, v_N), \tag{2.57}$$

where we used the kinematic relation in the third equality. Now, view R as a function of $v_i, i = 1, \cdots, N$ and minimize R with respect to $v_i, i = 1, \cdots, N$.

$$\frac{\partial R}{\partial v_i} = kx_i + \gamma_i v_i + \sum_{j \neq i} \frac{1}{2}(\gamma_{ij} + \gamma_{ji})(v_i - v_j) = 0 \text{ for } i = 1, \cdots, N. \tag{2.58}$$

Noting that $\gamma_{ij} = \gamma_{ji}$, we recover the dynamic equation (2.54). The principle that the true velocities should be the minimizer of the above function R is known as the *Onsager Variational Principle*, which has been advocated as a systematic way of deriving dynamic equations for soft condensed matter systems [9]. There are several possible advantages of this variational approach [41]. It is often easier to write down an energy relation (which is a scalar equality) than a dynamic equation. The dynamic equation can then be derived systematically. Equations derived in this way automatically satisfy the Onsager reciprocity principle. In the above computation, this is the statement that γ_{ij} should be symmetric. Finally, the variational principle is well-suited in the presence of constraints, as we shall see in our gel example below.

The mechanical model is described as in section 2.1 and section 2.2, in which we assume the *kinematic relations* to be (2.2), (2.30)-(2.33). The *kinematic constraints* include the imcompressibility in Ω_t (2.3) and in $\mathcal{R}_t$ (2.9). At the boundary of the gel region, we propose (2.11)-(2.13), and on the outer surface $\partial\mathbb{U}$, we propose (2.18).

Before stating the Onsager's variational principle, we introduce some notations. Let the potential energy

$$U = E_{\text{FH}} + E_{\text{elas}} = \int_{\Omega_t} \mathcal{W}_{\text{FH}}(\phi_1) + \phi_1 \mathcal{W}_{\text{elas}}(\mathcal{F}) d\mathbf{x}, \tag{2.59}$$

include elastic and Flory-Huggins energy in Ω_t, a representative form of the former could be (2.35), and the latter is defined by (2.36).

We neglect the inertial effects, namely let $\gamma_{1,2} = 0$ in (2.4), so the kinetic energy is not considered. We *denote* $\dot{U}$ as

$$\begin{aligned}
\dot{U} =& \frac{dU}{dt} \\
=& \int_{\Omega_t} \frac{d\mathcal{W}_{\text{FH}}}{d\phi_1} \frac{\partial \phi_1}{\partial t} + \nabla \cdot (\mathcal{W}_{\text{FH}} \mathbf{v}_1) d\mathbf{x} + \frac{d}{dt} \int_{\Omega} \phi_I \mathcal{W}_{\text{elas}}(F) d\mathbf{X} \\
=& \int_{\Omega_t} -\frac{d\mathcal{W}_{\text{FH}}}{d\phi_1} \nabla \cdot (\phi_1 \mathbf{v}_1) + \nabla \cdot (\mathcal{W}_{\text{FH}} \mathbf{v}_1) d\mathbf{x} + \int_{\Omega} \phi_I \frac{\partial \mathcal{W}_{\text{elas}}(F)}{\partial F} : \frac{\partial F}{\partial t} d\mathbf{X} \\
=& \int_{\Omega_t} -\frac{d\mathcal{W}_{\text{FH}}}{d\phi_1} \nabla \cdot (\phi_1 \mathbf{v}_1) + \nabla \cdot (\mathcal{W}_{\text{FH}} \mathbf{v}_1) + \phi_1 \frac{\partial \mathcal{W}_{\text{elas}}(\mathcal{F})}{\partial \mathcal{F}} : (\nabla \mathbf{v}_1 \mathcal{F}) d\mathbf{x}.
\end{aligned} \tag{2.60}$$

Here, we do not *define* $\dot{U}$ as in the first two lines; the "$\cdot$" symbol and the partial derivative symbol are only notations that are replaced by spatial derivatives from the kinematic relations (2.2), (2.32) and (2.33). The term $\dot{U}$ is only defined by the last line (2.60). As we will see later, when we introduce ion species, the same rule applies to the ionic energy and we will assume the reader understands the expression for $\dot{U}$ before presenting the proof.

We assume the network and fluid are both viscous, and there exists friction between the polymer and solvent in Ω_t. Let Rayleigh's dissipation function be

$$\begin{aligned} W = &\int_{\Omega_t} \left(\frac{1}{2}\kappa |\mathbf{v}_1 - \mathbf{v}_2|^2 + \sum_{i=1}^{2} \eta_i \left\| \nabla_S \mathbf{v}_i \right\|^2 \right) d\mathbf{x} + \int_{\mathcal{R}_t} \eta_{\mathrm{f}} \left\| \nabla_S \mathbf{v}_{\mathrm{f}} \right\|^2 d\mathbf{x} \\ &+ \int_{\Gamma_t} \frac{1}{2} \left(\eta_\perp w^2 + \eta_\parallel |\mathbf{q}|^2 \right) dS, \end{aligned} \tag{2.61}$$

the quadratic term with κ corresponds to friction, the quadratic terms with $\eta_{i,\mathrm{f}}$ correspond to viscosity, and the boundary terms correspond to interface friction. Now we may state the Onsager's variational result as follows.

Theorem 2.2. *Let* ϕ_1, ϕ_2 *be smooth functions that satisfy* (2.1)*,* U *be defined by* (2.36) *and* (2.59)*,* $\dot{U}$ *be defined through the kinematic relations* (2.2) *and* (2.30)-(2.33)*. Let*

$$Z \subset (C^2(\Omega_t))^2 \times C^2(\mathcal{R}_t) \tag{2.62}$$

be a subspace consisting of all elements $\{\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_{\mathrm{f}}\}$ *that the incompressible constraints* (2.3)*,* (2.9) *and boundary conditions* (2.11)-(2.13)*,* (2.18) *are satisfied. Suppose, for some* $\{\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_{\mathrm{f}}\}$*,* (2.4)*,* (2.8) *with* $\gamma_{1,2} = 0$*,* (2.34)-(2.45) *are all well defined and satisfied, then this* $\{\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_{\mathrm{f}}\}$ *minimizes*

$$R = \dot{U} + W$$

in Z*.*

Proof. We want to find the necessary conditions that an element of Z minimizes the energy dissipation rate R, subject to the incompressibility condition (2.3) and (2.9).

Accordingly, we try to minimize

$$\mathcal{R} = R - \int_{\Omega_t} p\nabla\cdot(\phi_1\mathbf{v}_1+\phi_2\mathbf{v}_2)d\mathbf{x} - \int_{\mathcal{R}_t} p\nabla\cdot\mathbf{v}_\mathrm{f}d\mathbf{x}.$$

instead of R. The set of minimizer $\{\mathbf{v}_{i,\mathrm{f}}\}$ has to satisfy

$$\frac{\delta\mathcal{R}}{\delta\mathbf{v}_i} = 0 \quad \text{for} \quad i=1,2,f.$$

Now we prove the equations above are equivalent to the force balance equations (2.4)($i=1,2$) and (2.8). Let $\mathcal{T}_{i,\mathrm{f}}$, $\mathcal{S}_g$, $\mathbf{f}_{i,\mathrm{f}}$, $\mathbf{g}_i$ be defined by (2.34), (2.38), (2.39), (2.41)-(2.43). First, we use (2.32),(2.60) and apply Reynolds transport formula to get

$$\begin{aligned}&\frac{d}{dt}\int_{\Omega_t}\mathcal{W}_\mathrm{FH}(\phi_1)+\mathcal{W}_\mathrm{elas}(\mathcal{F})d\mathbf{x}\\ &=\int_{\Omega_t}\left(\mathcal{W}_\mathrm{FH}-\phi_1\frac{\partial\mathcal{W}_\mathrm{FH}}{\partial\phi_1}\right)(\nabla\cdot\mathbf{v}_1)+\left(\phi_1\frac{\partial\mathcal{W}_\mathrm{elas}}{\partial\mathcal{F}}\mathcal{F}^T\right):(\nabla\mathbf{v}_1)d\mathbf{x}\\ &=-\int_{\Omega_t}(\nabla\cdot\mathcal{S}_g+\nabla\cdot\mathcal{T}_1^\mathrm{elas})\cdot\mathbf{v}_1d\mathbf{x}+\int_{\Gamma_t}\left(\mathcal{S}_g\mathbf{n}+\mathcal{T}_1^\mathrm{elas}\mathbf{n}\right)\cdot\mathbf{v}_1dS\end{aligned} \tag{2.63}$$

and use (2.34) and (2.42) to get

$$\int_{\Omega_t}\eta_i\left\|\nabla_S\mathbf{v}_i\right\|^2d\mathbf{x} = -\int_{\Omega_t}\left(\nabla\cdot\mathcal{T}_i^\mathrm{visc}\right)\cdot\mathbf{v}_id\mathbf{x}+\int_{\Gamma_t}\left(\mathcal{T}_i^\mathrm{visc}\mathbf{n}\right)\cdot\mathbf{v}_id\mathbf{x}$$

for $i=1,2$ and for $i=f$ when the domain is replaced by $\mathcal{R}_t$. Integrate the pressure terms by parts, and use (2.34) and (2.42) again, it follows

$$\begin{aligned}\mathcal{R}=&\int_{\Omega_t}-(\nabla\cdot(\mathcal{T}_1+\mathcal{S}_g))\cdot\mathbf{v}_1-(\nabla\cdot\mathcal{T}_2)\cdot\mathbf{v}_2+\frac{1}{2}\kappa|\mathbf{v}_1-\mathbf{v}_2|^2+(\phi_1\mathbf{v}_1+\phi_2\mathbf{v}_2)\cdot\nabla p\ d\mathbf{x}\\ &+\int_{\mathcal{R}_t}-(\nabla\cdot\mathcal{T}_f)\cdot\mathbf{v}_\mathrm{f}+\mathbf{v}_\mathrm{f}\cdot\nabla p\ d\mathbf{x}+\ A,\end{aligned} \tag{2.64}$$

where A stands for the integral of boundary terms

$$\begin{aligned}A=\int_{\Gamma_t}&(\mathcal{T}_1\mathbf{n}+\mathcal{S}_g\mathbf{n})\cdot\mathbf{v}_1+(\mathcal{T}_2\mathbf{n})\cdot\mathbf{v}_2-(\mathcal{T}_\mathrm{f}\mathbf{n})\cdot\mathbf{v}_\mathrm{f}\\ &-p^+(\phi_1\mathbf{v}_1+\phi_2\mathbf{v}_2)\cdot\mathbf{n}+p^-(\mathbf{v}_\mathrm{f}\cdot\mathbf{n})+\frac{1}{2}\left(\eta_\perp w^2+\eta_\parallel|\mathbf{q}|^2\right)dS,\end{aligned} \tag{2.65}$$

in which the indexes {+, -} denote evaluations on the Ω_t side and $\mathcal{R}_t$ side, respectively. Now take the partial derivative of $\mathcal{R}$ with respect to $\mathbf{v}_{1,2,\mathrm{f}}$, it is straightforward to reach (2.4) and (2.8).

To derive boundary conditions (2.16), (2.44)-(2.45), we use $\{\mathbf{v}_1+\epsilon a, \mathbf{v}_2+\epsilon b, \mathbf{v}_\mathrm{f}+\epsilon c\}$ instead of $\{\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_\mathrm{f}\}$, take derivative w.r.t. ϵ and let $\epsilon = 0$, it follows

$$\begin{aligned}\left.\frac{dA}{d\epsilon}\right|_{\epsilon=0} =& \int_{\Gamma_t} (\mathcal{T}_1\mathbf{n} + \mathcal{S}_g\mathbf{n} + \mathcal{T}_2\mathbf{n} - \mathcal{T}_f\mathbf{n} + [p]) \cdot a + (\mathcal{T}_2\mathbf{n}) \cdot (b-a) - (\mathcal{T}_\mathrm{f}\mathbf{n})\,(c-a) \\ &- \phi_2 p^+(b-a)\cdot\mathbf{n} + p^-(c-a)\cdot\mathbf{n} + \eta_\perp w \cdot (c-a)_\perp + \eta_\| q \cdot (c-a)_\| dS,\end{aligned}$$

Apply (2.12) and (2.13), to get

$$\begin{aligned}(c-a)_\perp &= \phi_2(b-a)_\perp; \\ (c-a)_\| &= (b-a)_\|.\end{aligned}$$

Therefore, one can further simplify and reach

$$\begin{aligned}\left.\frac{dA}{d\epsilon}\right|_{\epsilon=0} =& \int_{\Gamma_t} (\mathcal{T}_1\mathbf{n} + \mathcal{S}_g\mathbf{n} + \mathcal{T}_2\mathbf{n} - \mathcal{T}_\mathrm{f}\mathbf{n} + [p]) \cdot a + (\mathcal{T}_2\mathbf{n} - \phi_2\,[p] - \phi_2\mathcal{T}_\mathrm{f}\mathbf{n} + \phi_2\eta_\perp w) \\ &\cdot (b-a)_\perp + \big((\mathcal{T}_2\mathbf{n} - \mathcal{T}_\mathrm{f}\mathbf{n})_\| + \eta_\|\mathbf{q}\big) \cdot (b-a)_\| dS.\end{aligned}$$

Since a, b are arbitrary (c is determined when they are chosen), the following must hold:

$$\begin{aligned}\mathcal{T}_1\mathbf{n} + \mathcal{S}_g\mathbf{n} + \mathcal{T}_2\mathbf{n} - \mathcal{T}_\mathrm{f}\mathbf{n} + [p] = 0, \\ \mathbf{n}\cdot(\mathcal{T}_2\mathbf{n}) - \phi_2\,[p] - \phi_2\mathbf{n}\cdot(\mathcal{T}_\mathrm{f}\mathbf{n}) + \phi_2\eta_\perp w = 0, \\ (\mathcal{T}_2\mathbf{n} - \mathcal{T}_\mathrm{f}\mathbf{n})_\| + \eta_\|\mathbf{q} = 0.\end{aligned}$$

The first and second equations above are (2.16) and (2.44), and

$$(\mathcal{T}_2\mathbf{n} - \mathcal{T}_\mathrm{f}\mathbf{n})_\| + \eta_\|\mathbf{q} = -(\mathcal{T}_1\mathbf{n})_\| + \eta_\|\mathbf{q} = 0,$$

which is (2.45). Now we have proved the nessessity part. Notice $R = \dot{U} + W$ is quardratic and positive definite in $\{\mathbf{v}_{i,\mathrm{f}}\}$, hence the set must be *the* minimizer. The proof is complete. □

2.4 One-dimensional stability analysis

In this section, we will consider the swelling dynamics of a one-dimensional mechanical gel. Our goals are to find steady state solutions, to find the minimum decay rate of small perturbations, and to discuss the behaviour of the minimum decay rate as permeability changes.

Let $\mathbb{U} = (0, L) \in \mathbb{R}$ be the region containing the gel and fluid, let $\Omega_t = (0, a)$, $a(t) < L$ be the domain of the polymer network, in which L being length of the domain is fixed. The gel is fixed at $x = 0$ and moves at $x = a(t)$ with velocity $\mathbf{v}_1$. The deformation gradient reduces to a positive number which is proportional to the inverse of ϕ_1, hence we can let $f = f(\phi_1)$ to be the total free energy density at each point, including the elastic energy and Flory-Huggins energy. We always assume f to be strictly convex and

$$\frac{d}{d\phi_1}\left(\frac{f(\phi_1)}{\phi_1}\right)\Bigg|_{\phi_1=0^+} < 0, \quad \frac{d}{d\phi_1}\left(\frac{f(\phi_1)}{\phi_1}\right)\Bigg|_{\phi_1=1^-} > 0 \tag{2.66}$$

which indicates the total free energy increases when the gel is exceedingly stretched or compressed. The constitutive equations (2.2)-(2.4), (2.8) and boundary conditions (2.11)-(2.13), (2.16), (2.18), (2.44)-(2.45) are stated as follows.

At $x = 0$,

$$v_1 = v_2 = 0; \tag{2.67}$$

in $(0, a)$,

$$\phi_1 + \phi_2 = 1; \tag{2.68}$$

$$\frac{\partial \phi_i}{\partial t} + (v_i\phi_i)_x = 0 \quad \text{for} \ \ i = 1, 2; \tag{2.69}$$

$$(\phi_1 v_1 + \phi_2 v_2)_x = 0; \tag{2.70}$$

$$(\eta_1 v_{1,x})_x + (f - \phi_1 f')_x - \phi_1 p_x + \kappa(v_2 - v_1) = 0; \tag{2.71}$$

$$(\eta_2 v_{2,x})_x - \phi_2 p_x + \kappa(v_1 - v_2) = 0 \tag{2.72}$$

while at $x = a$

$$v_{\mathrm{f}} - v_1 = \phi_2(v_2 - v_1); \tag{2.73}$$

$$\eta_{\mathrm{f}}(v_{\mathrm{f}})_x - \eta_1(v_1)_x - (f - \phi_1 f') - \eta_2(v_2)_x + [p] = 0; \tag{2.74}$$

$$\eta_\perp(v_{\mathrm{f}} - v_1) = \eta_{\mathrm{f}}(v_{\mathrm{f}})_x - \phi_2^{-1}\eta_2(v_2)_x + [p]\,; \tag{2.75}$$

and in (a, L),

$$(v_{\mathrm{f}})_x = 0; \tag{2.76}$$

$$(\eta_{\mathrm{f}} v_{\mathrm{f},x})_x - p_x = 0; \tag{2.77}$$

while at $x = L$

$$v_{\mathrm{f}} = 0. \tag{2.78}$$

Moreover,

$$\dot{a} = v_1(x = a). \tag{2.79}$$

Note also that (2.13) and (2.45) becomes trivial in the one-dimensional case.

We first consider the equations for the surrounding fluid. From (2.76) and (2.78) it follows $v_{\mathrm{f}} \equiv 0$ in (a, L), and from (2.77) p is constant in (a, L), we set $p = 0$ in (a, L). The trivial solutions of v_{f} and p indicate that there is little interest outside the polymer network, hence we restrict our focus on the domain of gel $[0, a]$ from now on.

From (2.68), (2.70) and (2.73), it follows

$$\phi_1 v_1 + \phi_2 v_2 = 0 \quad \text{in } (0, a), \text{ or } \quad v_2 = -\frac{\phi_1 v_1}{1 - \phi_1}. \tag{2.80}$$

Adding (2.71) and (2.72) and integrating on x, it follows

$$p = \eta_1 (v_1)_x + \eta_2 (v_2)_x + (f - \phi_1 f') + g(t) \quad \text{in } (0, a), \tag{2.81}$$

and $g(t) \equiv 0$ from (2.74). Together with $\phi_2 = 1 - \phi_1$, we derive equations for $\{\phi_1, v_1\}$:

$$\begin{gathered} \frac{\partial \phi_1}{\partial t} + (\phi_1 v_1)_x = 0; \\ (1 - \phi_1)(\eta_1 v_{1,x})_x + \phi_1 \left(\eta_2 \left(\frac{\phi_1 v_1}{1 - \phi_1} \right)_x \right)_x + (1 - \phi_1)(f - \phi_1 f')_x = \frac{\kappa v_1}{1 - \phi_1} \end{gathered} \tag{2.82}$$

in $(0, a)$, and boundary conditions

$$\begin{gathered} v_1 = 0 \quad \text{at} \quad x = 0; \\ -\eta_\perp v_1 = \eta_1 (v_1)_x + \frac{\phi_1}{1 - \phi_1} \eta_2 \left(\frac{\phi_1 v_1}{1 - \phi_1} \right)_x + (f - \phi_1 f') \quad \text{at} \quad x = a; \\ \dot{a} = v_1(x = a). \end{gathered} \tag{2.83}$$

2.4.1 Steady state solutions

Steady state solutions occur when there is no movement. We are only interested in the generic cases that the gel does not expand and occupy the whole domain. Let $v_1 \equiv 0$ in (2.82), then the solution of ϕ_1 must satisfy

$$\frac{\partial \phi_1}{\partial t} = 0; \ (f(\phi_1) - \phi_1 f'(\phi_1))_x = -\phi_1 (\phi_1)_x f''(\phi_1) = 0, \ 0 < \phi_1(x) < 1.$$

Since our energy density function $f(\phi_1)$ is assumed to be strictly convex for $0 < \phi_1 < 1$, the equilibrium of the system is a constant solution $\phi_1 \equiv \phi_0$, where ϕ_0 is determined by (2.81), namely

$$f(\phi_0) - \phi_0 f'(\phi_0) = 0. \tag{2.84}$$

It is easy to see there exists a unique solution to (2.84), from monotonicity of ϕ_1 and (2.66).

2.4.2 Minimum decay rate near the equilibria

We start with equations (2.82) and boundary conditions (2.83) for $\{v_1, \phi_1\}$. Let $\phi_1 = \phi_0, v_1 = 0$ be an equilibrium, and the reference domain of the polymer network be $(0, a)$. Consider a small perturbation

$$x = \varphi_t(X) = X + \epsilon u(X,t) + O(\epsilon^2), \quad \epsilon \ll 1, \tag{2.85}$$

where $\|u\|_{C^2} < 1$. This ensures φ_t is strictly increasing and second derivative has order ϵ. Then

$$\frac{\partial x}{\partial X} = 1 + \epsilon \frac{\partial u}{\partial X} + O(\epsilon^2),$$

and from (2.33)

$$\begin{aligned} \phi_1 &= \phi_0 \left(\frac{\partial \varphi_t}{\partial X} \right)^{-1} = \phi_0 \left(1 - \epsilon \frac{\partial u}{\partial X} \right) + O(\epsilon^2); \\ v_1 &= \frac{\partial x}{\partial t} = \epsilon \frac{\partial u}{\partial t} + O(\epsilon^2). \end{aligned} \tag{2.86}$$

Since $\partial/\partial X = \partial/\partial x \cdot (1 + \epsilon u_X)$, we linearize (2.82) under the current configuration, and derive the equation involving only $O(\epsilon)$ terms as

$$Hu_{txx} + \phi_0^2 f''(\phi_0) u_{xx} = \frac{\kappa u_t}{(1-\phi_0)^2}, \quad H = \eta_1 + \eta_2 \frac{\phi_0^2}{(1-\phi_0)^2} \tag{2.87}$$

is the mixed viscosity coefficient. For the boundary conditions, we apply (2.86) to (2.83) at $x = \epsilon u(0,0)$ and $x = a + \epsilon u(L,0)$. Using Talor expansion, we can find the approximated boundary conditions at $x = 0$ and $x = a$. It is easy to see the differences are $O(\epsilon^2)$ terms which are negligible, hence we summarize the linearized boundary conditions as follows:

$$\begin{aligned} u_t = 0 \quad \text{or} \quad u = 0 \quad &\text{at} \quad x = 0; \\ -\eta_\perp u_t = Hu_{tx} + \phi_0^2 f''(\phi_0) u_x \quad &\text{at} \quad x = a. \end{aligned} \tag{2.88}$$

The equations (2.87)-(2.88) satisfy a linearized version of energy dissipation identity. Multiply (2.87) by u_t and integrate over $(0, a)$, we derive

$$\begin{aligned} &\frac{d}{dt}\left(\frac{1}{2}\phi_0^2 f''(\phi_0) \int_0^a u_x^2 dx\right) \\ =& -H \int_0^a (u_{tx})^2 dx - \frac{\kappa}{(1-\phi_0)^2} \int_0^a u_t^2 dx - \eta_\perp u_t(a)^2. \end{aligned} \tag{2.89}$$

To find the minimum decay rate, we write $u(x,t)$ as the infinite sum of eigenfunctions:

$$u(x,t) = \sum_k a_k e^{-\lambda_k t} \omega_k(x). \tag{2.90}$$

Then (2.87) and (2.88) for the k-th term are

$$\begin{aligned} (\lambda_k H - \phi_0^2 f''(\phi_0))\omega_k'' = \frac{\lambda_k \kappa}{(1-\phi_0)^2}\omega_k \quad &\text{in} \quad (0,a); \\ \omega_k = 0 \quad &\text{at} \quad x = 0; \\ -\lambda_k \eta_\perp \omega_k = \left(\lambda_k H - \phi_0^2 f''(\phi_0)\right)\omega_k' \quad &\text{at} \quad x = a. \end{aligned}$$

Let λ be an eigenvalue. If $\lambda = 0$, we have

$$\omega_k'' = 0, \quad \text{and} \;\; \omega_k' = 0, \tag{2.91}$$

and $\omega_k = 0$. In the following we assume $\lambda \neq 0$. The only possible situation is when $\lambda H - \phi_0^2 f''(\phi_0) < 0$ and $\lambda > 0$. Let

$$\begin{aligned} M^2 &= -\frac{\lambda\kappa}{(1-\phi_0)^2(\lambda H - \phi_0^2 f''(\phi_0))}, \ M > 0; \\ B &= -\frac{\lambda\eta_\perp}{\lambda H - \phi_0^2 f''(\phi_0)} > 0, \end{aligned} \tag{2.92}$$

and let

$$\omega_k(x) = \alpha\cos(Mx) + \beta\sin(Mx).$$

Some direct computation yields the following equation which implicitly determines the eigenvalues:

$$\cot(Ma) = \frac{B}{M} = \frac{(1-\phi_0)\eta_\perp}{\sqrt{\kappa}} \cdot \sqrt{\frac{\lambda}{\phi_0^2 f''(\phi_0) - \lambda H}}. \tag{2.93}$$

We summarize the asymptotic behavior of the smallest eigenvalue as parameters $\eta_\perp$, H and a change. The proofs are straightforward and we omit them.

Theorem 2.3. *Let the perturbation function $u(x,t)$ be defined by (2.90) and $\lambda = \lambda_1$ be the smallest eigenvalue satisfying (2.93) where $M(\lambda)$ and $B(\lambda)$ are defined by (2.92). We change one variable of $\{\eta_\perp, H, a\}$ and fix the others each time, and λ_1 behaviors in the following manner:*
(i) As $\eta_\perp \to 0$,

$$\lambda_1 \to \frac{\phi_0^2 f''(\phi_0)}{\frac{4\kappa a^2}{(1-\phi_0)^2(\pi^2)^-} + H}.$$

In particular, if $\eta_\perp = 0$, which means fully permeable,

$$\lambda_k = \frac{\phi_0^2 f''(\phi_0)}{\frac{4\kappa a^2}{(1-\phi_0)^2 k^2\pi^2} + H} \quad \textit{for} \ \ k \in \mathbb{N}.$$

(ii) As $\eta_\perp \to \infty$, $\lambda_1 \to 0+$. In particular, if $\eta_\perp = \infty$, which means impermeable, $\lambda_1 = 0$.
(iii) As $H \to 0$, (2.93) becomes

$$\cot(Ma) = C \cdot \sqrt{\lambda}, \ \ \textit{in which} \ \ C = \frac{(1-\phi_0)\eta_\perp}{\phi_0\sqrt{\kappa f''(\phi_0)}}.$$

(iv) As a goes from 0 to ∞, λ_1 goes from $H^{-1}\phi_0^2 f''(\phi_0)$ to 0 monotonically.

Remark 2.1. *In (i), let $\eta_\perp = 0$,*

$$\lambda_1 = \frac{\phi_0^2 f''(\phi_0)}{\frac{4\kappa a^2}{(1-\phi_0)^2\pi^2} + H}. \tag{2.94}$$

can be treated as the principal eigenvalue of the polymer phase (PEP). It is also important in the ionic case.

Chapter 3

Polyelectrolyte gels

3.1 Electrodiffusion of Ions

We now consider the incorporation of diffusing ionic species into the model. Let $c_k, k = 1, \cdots, N$ be the concentrations of ionic species of interest and let z_k be the valence of each ionic species. These electrolytes are present in the solvent as well as in the outside fluid. We define c_k as being concentrations *with respect to the solvent*, and not with respect to unit volume. The polymer network carries a charge density of $\rho_p \phi_1$ per unit volume, where ρ_p is a constant. Now, define $\mathcal{W}_{\text{ion}}$ as follows:

$$\mathcal{W}_{\text{ion}} = k_B T \sum_{k=1}^{N} c_k \ln c_k, \tag{3.1}$$

where $k_B T$ is the Boltzmann constant times absolute temperature. The quantity $\mathcal{W}_{\text{ion}}$ is the entropic free energy of ions per unit volume of solvent or fluid. Much of the calculations to follow do not depend on the above specific form of $\mathcal{W}_{\text{ion}}$, but this is the most commonly used form. Using this, we define the chemical potential μ_k of the k-th ionic species as:

$$\mu_k = \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} + q z_k \psi = k_B T \ln c_k + q z_k \psi + k_B T. \tag{3.2}$$

where q is the elementary charge and ψ is the electrostatic potential, defined in both Ω_t and $\mathcal{R}_t$. In Ω_t, the concentrations c_k satisfy:

$$\begin{aligned}\frac{\partial}{\partial t}(\phi_2 c_k) + \nabla\cdot(\mathbf{v}_2\phi_2 c_k) &= \nabla\cdot\left(\frac{D_k c_k}{k_B T}\nabla\mu_k\right)\\ &= \nabla\cdot\left(D_k\left(\nabla c_k + \frac{q z_k c_k}{k_B T}\nabla\psi\right)\right),\end{aligned} \tag{3.3}$$

where $D_k > 0, k = 1, \cdots, N$ are the diffusion coefficients of the ions. The diffusion coefficients may be functions of ϕ_2, in which case we suppose that they are smooth bounded functions of ϕ_2. Note that the choice (3.1) for $\mathcal{W}_{\text{ion}}$ leads to linear diffusion. We point out here that our choice of the function $\mathcal{W}_{\text{ion}}$ resulted in ionic diffusion being proportional to the gradient of c_k, not $\phi_2 c_k$. Recall that c_k is the concentration per unit solvent volume whereas $\phi_2 c_k$ is concentration per unit volume. There are models in the literature in which ionic diffusion is proportional to the gradient of $\phi_2 c_k$ instead of c_k. Our choice stems from the view that, since ions are dissolved in water (solvent), it can only diffuse within the water phase.

In the fluid region $\mathcal{R}_t$, the concentrations satisfy:

$$\frac{\partial c_k}{\partial t} + \nabla\cdot(\mathbf{v}_{\text{f}} c_k) = \nabla\cdot\left(\frac{D_k c_k}{k_B T}\nabla\mu_k\right). \tag{3.4}$$

In Ω_t and in $\mathcal{R}_t$, the ions diffuse and drift down the electrostatic potential gradient and are advected by the local fluid flow. The electrostatic potential ψ satisfies the Poisson equation:

$$-\nabla\cdot(\epsilon\nabla\psi) = \begin{cases}\phi_1\rho_p + \sum_{k=1}^N q z_k \phi_2 c_k & \text{in } \Omega_t\\ \sum_{k=1}^N q z_k c_k & \text{in } \mathcal{R}_t\end{cases} \tag{3.5}$$

where ϵ is the dielectric constant. The dielectric constant in the gel Ω_t may well be different from that inside $\mathcal{R}_t$. We assume that ϵ may be a (smooth and bounded) function of ϕ_1 in Ω_t and remains constant in $\mathcal{R}_t$.

If we set the advective velocities to 0, equations (3.3), (3.4) and (3.5) are nothing other than the Poisson-Nernst-Planck system [32]. In many practical cases, the dielectric constant is "small" and it is an excellent approximation to let $\epsilon \to 0$ in the above. We shall discuss this electroneutral limit in Section 3.2.

We set the forces $\mathbf{f}_1$ and $\mathbf{f}_2$ as follows:

$$\begin{aligned} \mathbf{f}_1 &= \mathbf{f}_1^{\text{elec}} = -\rho_p \phi_1 \nabla\psi, \\ \mathbf{f}_2 &= \mathbf{f}_2^{\text{elec}} = -\left(\sum_{k=1}^N q z_k \phi_2 c_k\right)\nabla\psi, \\ \mathbf{f}_{\text{f}} &= \mathbf{f}_{\text{f}}^{\text{elec}} = -\left(\sum_{k=1}^N q z_k c_k\right)\nabla\psi. \end{aligned} \tag{3.6}$$

These are the electrostatic forces acting on the polymer network and the fluid. We prescribe the pressure difference as follows:

$$p_\Delta = p_\Delta^{\text{FH}} + p_\Delta^{\text{elec}},\ p_\Delta^{\text{FH}} = \frac{d\mathcal{W}_{\text{FH}}}{d\phi_1},\ p_\Delta^{\text{elec}} = -\frac{1}{2}\frac{d\epsilon}{d\phi_1}\left|\nabla\psi\right|^2. \tag{3.7}$$

The term p_Δ^{elec} is known as the Helmholtz force [24]. We point out that the definition of p_Δ^{elec} is symmetric with respect to ϕ_1 and ϕ_2, as can be seen by an argument identical to (2.37).

With the following definitions for $\mathcal{S}_g$ and $\mathcal{S}_{\text{f}}$, conditions (2.10) and (2.6) are satisfied.

$$\begin{aligned} \mathcal{S}_g &= \mathcal{S}_g^{\text{FH}} + \mathcal{S}_g^{\text{elec}},\ \mathcal{S}_g^{\text{elec}} = \mathcal{S}_g^{\text{mw}} + \frac{1}{2}\phi_1\frac{d\epsilon}{d\phi_1}|\nabla\psi|^2 I, \\ \mathcal{S}_{\text{f}} &= \mathcal{S}_{\text{f}}^{\text{elec}} = \mathcal{S}_{\text{f}}^{\text{mw}},\ \mathcal{S}_{g,f}^{\text{mw}} \equiv \epsilon\left(\nabla\psi\otimes\nabla\psi - \frac{1}{2}|\nabla\psi|^2 I\right) \end{aligned} \tag{3.8}$$

where $\mathcal{S}_g^{\text{FH}}$ was given in (2.39). The tensor $\mathcal{S}^{\text{mw}}$ is the standard Maxwell stress tensor in the absence of a magnetic field [42, 24]. Inside the gel there is an additional term to account for the non-uniformity of the dielectric constant. We prescribe $\mathbf{g}_i$ as in (2.41). We shall also adopt the boundary conditions (2.44) and (2.45).

We must provide (3.3), (3.4) and (3.5) with boundary conditions. We require that the ionic concentrations c_k the flux across Γ_t be continuous:

$$[c_k] = 0, \tag{3.9}$$

$$\left((\mathbf{v}_{\text{f}} - \mathbf{v}_1)c_k - \frac{D_k c_k}{k_B T}\nabla\mu_k\right)\cdot\mathbf{n}\bigg|_{\mathcal{R}_t} = \left((\mathbf{v}_2 - \mathbf{v}_1)\phi_2 c_k - \frac{D_k c_k}{k_B T}\nabla\mu_k\right)\cdot\mathbf{n}\bigg|_{\Omega_t} \equiv j_k. \tag{3.10}$$

We have named the concentration flux j_k for later convenience.

For the electrostatic potential ψ, we require:

$$[\psi] = [\epsilon \nabla \psi \cdot \mathbf{n}] = 0. \tag{3.11}$$

Finally, at the outer boundary of $\mathbb{U}$, we require the following no-flux boundary conditions for both c_k and ψ, on $\partial\mathbb{U}$:

$$\left(\mathbf{v}_{\mathrm{f}} c_k - \frac{D_k c_k}{k_B T} \nabla \mu_k \right) \cdot \mathbf{n} = 0, \tag{3.12}$$

$$\epsilon \nabla \psi \cdot \mathbf{n} = 0. \tag{3.13}$$

It is easily checked that the above boundary conditions lead to conservation of total amount of ions. For the Poisson equation to have a solution, we must require, by the Fredholm alternative, that:

$$\int_{\mathcal{R}_t} \left(\sum_{k=1}^{N} q z_k c_k \right) d\mathbf{x} + \int_{\Omega_t} \left(\sum_{k=1}^{N} q z_k c_k + \rho_p \phi_1 \right) d\mathbf{x} = 0. \tag{3.14}$$

The electrostatic potential ψ is only determined up to an additive constant. Given that the amount of ions and the amount of polymer (integral of ϕ_1) are conserved, the above condition will be satisfied so long as it is satisfied at the initial time.

We now turn to linear momentum and free energy balance. We point out that a related energy identity for a different system was proved recently in [29].

Theorem 3.1. *Let* $\phi_i, \mathbf{v}_i$ *and* $\mathbf{v}_{\mathrm{f}}$ *be smooth functions satisfying* (2.1), (2.2), (2.4), (2.8), (2.9), (2.12), (2.13), (2.16), (2.18), (2.44), (2.45) *and* c_k *and* ψ *are smooth functions satisfying* (3.3), (3.4), (3.5), (3.10) *and* (3.11). *Suppose the stress, pressure difference and the body forces are given by* (2.34), (2.42), (3.7), (3.6) *and* (2.41). *Then, we have total linear momentum conservation in the sense of Lemma* 2.1. *We also have the following free energy dissipation identity:*

$$\begin{aligned}
&\frac{d}{dt}(E_{\mathrm{KE}} + E_{\mathrm{elas}} + E_{\mathrm{FH}} + E_{\mathrm{ion}} + E_{\mathrm{elec}}) = -I_{\mathrm{visc}} - I_{\mathrm{diff}} - J_{\mathrm{visc}}, \\
&E_{\mathrm{ion}} = \int_{\Omega_t} \phi_2 \mathcal{W}_{\mathrm{ion}} d\mathbf{x} + \int_{\mathcal{R}_t} \mathcal{W}_{\mathrm{ion}} d\mathbf{x}, \quad E_{\mathrm{elec}} = \int_{\mathbb{U}} \frac{1}{2} \epsilon \left| \nabla \psi \right|^2 d\mathbf{x}, \\
&I_{\mathrm{diff}} = \int_{\mathbb{U}} \frac{D_k c_k}{k_B T} \left| \nabla \mu_k \right|^2 d\mathbf{x},
\end{aligned} \tag{3.15}$$

where $E_{\mathrm{KE}}, E_{\mathrm{elas}}, E_{\mathrm{FH}}, I_{\mathrm{visc}}$ *and* J_{visc} *were defined in* (2.48).

Proof. Given (2.41), linear momentum conservation is immediate from Lemma 2.1. We now turn to (3.15). Substitute (2.34), (2.42)-(2.45) into (2.25), Using Lemma 2.2 and the results of Theorem 2.1, we have:

$$\begin{aligned} \frac{d}{dt}(E_{\mathrm{KE}} + E_{\mathrm{elas}} + E_{\mathrm{FH}}) &= -I_{\mathrm{visc}} - J_{\mathrm{visc}} + P_{\mathrm{elec}}, \\ P_{\mathrm{elec}} = \int_{\Omega_t} &(-\phi_1 \nabla p_\Delta^{\mathrm{elec}} + \mathbf{f}_1^{\mathrm{elec}}) \cdot \mathbf{v}_1 + \mathbf{f}_2^{\mathrm{elec}} \cdot \mathbf{v}_2) d\mathbf{x} \\ &+ \int_{\mathcal{R}_t} \mathbf{f}_{\mathrm{f}}^{\mathrm{elec}} \cdot \mathbf{v}_{\mathrm{f}} d\mathbf{x} - \int_{\Gamma_t} ((\mathcal{S}_g^{\mathrm{elec}} - \mathcal{S}_{\mathrm{f}}^{\mathrm{elec}})\mathbf{n}) \cdot \mathbf{v}_1 dS. \end{aligned} \tag{3.16}$$

Comparing this with (3.15), we must show that:

$$\frac{d}{dt}(E_{\mathrm{ion}} + E_{\mathrm{elec}}) = -I_{\mathrm{diff}} - P_{\mathrm{elec}}. \tag{3.17}$$

First, multiply (2.2) with $i = 1$ by $\rho_p \psi$ and integrate in Ω_t:

$$\begin{aligned} &\int_{\Omega_t} \rho_p \psi \left(\frac{\partial \phi_1}{\partial t} + \nabla \cdot (\phi_1 \mathbf{v}_1) \right) d\mathbf{x} \\ =&\frac{d}{dt} \int_{\Omega_t} \rho_p \phi_1 \psi d\mathbf{x} - \int_{\Omega_t} \rho_p \phi_1 \frac{\partial \psi}{\partial t} d\mathbf{x} + \int_{\Omega_t} \mathbf{f}_1^{\mathrm{elec}} \cdot \mathbf{v}_1 d\mathbf{x} = 0, \end{aligned} \tag{3.18}$$

where we integrated by parts and used the fact that ρ_p is a constant. Note that we used (3.6) to rewrite the third integral in terms of $\mathbf{f}_1^{\mathrm{elec}}$. Multiply (3.3) by μ_k and integrate over Ω_t. The left hand side gives:

$$\begin{aligned} &\int_{\Omega_t} \left(\sum_{k=1}^N \mu_k \left(\frac{\partial}{\partial t}(\phi_2 c_k) + \nabla \cdot (\mathbf{v}_2 \phi_2 c_k) \right) \right) d\mathbf{x} \\ =&\int_{\Omega_t} \left(\sum_{k=1}^N \frac{\partial \mathcal{W}_{\mathrm{ion}}}{\partial c_k} \left(\frac{\partial}{\partial t}(\phi_2 c_k) + \nabla \cdot (\mathbf{v}_2 \phi_2 c_k) \right) \right) d\mathbf{x} \\ +&\int_{\Omega_t} \left(\sum_{k=1}^N q z_k \psi \left(\frac{\partial}{\partial t}(\phi_2 c_k) + \nabla \cdot (\mathbf{v}_2 \phi_2 c_k) \right) \right) d\mathbf{x} = S_1 + S_2. \end{aligned} \tag{3.19}$$

To simplify S_1, note that:

$$\begin{aligned}
&\sum_{k=1}^{N} \frac{\partial \mathcal{W}_{\rm ion}}{\partial c_k}\left(\frac{\partial}{\partial t}(\phi_2 c_k) + \nabla\cdot(\mathbf{v}_2\phi_2 c_k)\right) = \sum_{k=1}^{N}\phi_2\frac{\partial \mathcal{W}_{\rm ion}}{\partial c_k}\left(\frac{\partial c_k}{\partial t} + \mathbf{v}_2\cdot\nabla c_k\right)\\
=&\phi_2\left(\frac{\partial}{\partial t}\mathcal{W}_{\rm ion} + \mathbf{v}_2\cdot\nabla\mathcal{W}_{\rm ion}\right) = \frac{\partial}{\partial t}(\phi_2\mathcal{W}_{\rm ion}) + \nabla\cdot(\mathbf{v}_2\phi_2\mathcal{W}_{\rm ion})
\end{aligned} \tag{3.20}$$

where we used (2.2) with $i = 2$ in the second and third equalities. Therefore, we have:

$$\begin{aligned}
S_1 &= \int_{\Omega_t} \frac{\partial}{\partial t}(\phi_2\mathcal{W}_{\rm ion}) + \nabla\cdot(\mathbf{v}_2\phi_2\mathcal{W}_{\rm ion}) d\mathbf{x}\\
&= \frac{d}{dt}\int_{\Omega_t}\phi_2\mathcal{W}_{\rm ion} d\mathbf{x} + \int_{\Gamma_t}\phi_2\mathcal{W}_{\rm ion}(\mathbf{v}_2-\mathbf{v}_1)\cdot\mathbf{n} dS.
\end{aligned} \tag{3.21}$$

where we integrated by parts in the second equality. Let us now turn to S_2. Integrating by parts, we obtain:

$$\begin{aligned}
S_2 = &\frac{d}{dt}\int_{\Omega_t}\left(\psi\sum_{k=1}^{N} q z_k \phi_2 c_k\right) d\mathbf{x} - \int_{\Omega_t}\left(\frac{\partial\psi}{\partial t}\sum_{k=1}^{N} q z_k\phi_2 c_k\right) d\mathbf{x}\\
&+ \int_{\Omega_t}\mathbf{f}_2^{\rm elec}\cdot\mathbf{v}_2 d\mathbf{x} + \int_{\Gamma_t}\left(\psi\sum_{k=1}^{N} q z_k c_k\phi_2(\mathbf{v}_2-\mathbf{v}_1)\cdot\mathbf{n}\right) d\mathbf{x},
\end{aligned} \tag{3.22}$$

where we used (3.6) to write the third integral in terms of $\mathbf{f}_2^{\rm elec}$. If we multiply the right hand side of (3.3) by μ_k, sum in k and integrate in Ω_t, we have:

$$\begin{aligned}
&\int_{\Omega_t}\left(\sum_{k=1}^{N}\mu_k\nabla\cdot\left(\frac{D_k c_k}{k_B T}\nabla\mu_k\right)\right) d\mathbf{x}\\
=&\int_{\Gamma_t}\left(\sum_{k=1}^{N}\mu_k\frac{D_k c_k}{k_B T}\nabla\mu_k\cdot\mathbf{n}\right) dS - \int_{\Omega_t}\left(\sum_{k=1}^{N}\frac{D_k c_k}{k_B T}\left|\nabla\mu_k\right|^2\right) d\mathbf{x}.
\end{aligned} \tag{3.23}$$

Collecting (3.18), (3.19), (3.21)-(3.23), we have:

$$
\begin{aligned}
&\frac{d}{dt}\int_{\Omega_t}\left(\phi_2\mathcal{W}_{\text{ion}}+\psi\left(\phi_1\rho_p+\sum_{k=1}^N qz_k\phi_2c_k\right)\right)d\mathbf{x}\\
&-\int_{\Omega_t}\left(\frac{\partial\psi}{\partial t}\left(\phi_1\rho_p+\sum_{k=1}^N qz_k\phi_2c_k\right)\right)d\mathbf{x}\\
&=-\int_{\Gamma_t}\left(\sum_{k=1}^N j_k\mu_k-\left(\sum_{k=1}^N c_k\frac{\partial\mathcal{W}_{\text{ion}}}{\partial c_k}-\mathcal{W}_{\text{ion}}\right)w\right)dS\\
&-\int_{\Omega_t}\left(\sum_{k=1}^N\frac{D_kc_k}{k_BT}\left|\nabla\mu_k\right|^2\right)d\mathbf{x}-\int_{\Omega_t}(\mathbf{f}_1^{\text{elec}}\cdot\mathbf{v}_1+\mathbf{f}_2^{\text{elec}}\cdot\mathbf{v}_2)d\mathbf{x}
\end{aligned}
\tag{3.24}
$$

where we used (2.12) and (3.10). Multiplying (3.4) by μ_k, taking the sum in k and integrating over $\mathcal{R}_t$, we obtain, similarly to (3.24):

$$
\begin{aligned}
&\frac{d}{dt}\int_{\mathcal{R}_t}\left(\mathcal{W}_{\text{ion}}+\psi\sum_{k=1}^N qz_kc_k\right)d\mathbf{x}-\int_{\mathcal{R}_t}\left(\frac{\partial\psi}{\partial t}\sum_{k=1}^N qz_kc_k\right)d\mathbf{x}\\
=&\int_{\Gamma_t}\left(\sum_{k=1}^N j_k\mu_k-\left(\sum_{k=1}^N c_k\frac{\partial\mathcal{W}_{\text{ion}}}{\partial c_k}-\mathcal{W}_{\text{ion}}\right)w\right)dS\\
-&\int_{\mathcal{R}_t}\left(\sum_{k=1}^N\frac{D_kc_k}{k_BT}\left|\nabla\mu_k\right|^2\right)d\mathbf{x}-\int_{\mathcal{R}_t}\mathbf{f}_{\text{f}}^{\text{elec}}\cdot\mathbf{v}_{\text{f}}d\mathbf{x}.
\end{aligned}
\tag{3.25}
$$

Adding (3.24) and (3.25) and using the fact that c_k and ψ are continuous across Γ_t, we have,:

$$
\begin{aligned}
&\frac{d}{dt}E_{\text{ion}}-\frac{d}{dt}\int_{\mathbb{U}}\psi\nabla\cdot(\epsilon\nabla\psi)d\mathbf{x}+\int_{\mathbb{U}}\frac{\partial\psi}{\partial t}\nabla\cdot(\epsilon\nabla\psi)d\mathbf{x}\\
=&-I_{\text{diff}}-P_{\text{elec}}-\int_{\Omega_t}(\phi_1\mathbf{v}_1)\cdot\nabla p_{\Delta}^{\text{elec}}d\mathbf{x}-\int_{\Gamma_t}((\mathcal{S}_g^{\text{elec}}-\mathcal{S}_{\text{f}}^{\text{elec}})\mathbf{n})\cdot\mathbf{v}_1dS.
\end{aligned}
\tag{3.26}
$$

Now consider the two integrals on the first line of (3.26):

$$
-\frac{d}{dt}\int_{\mathbb{U}}\psi\nabla\cdot(\epsilon\nabla\psi)d\mathbf{x}=\frac{d}{dt}\int_{\mathbb{U}}\epsilon|\nabla\psi|^2d\mathbf{x}+\frac{d}{dt}\int_{\Gamma_t}\left[\psi\epsilon\frac{\partial\psi}{\partial\mathbf{n}}\right]dS=\frac{d}{dt}\int_{\mathbb{U}}\epsilon|\nabla\psi|^2d\mathbf{x}
\tag{3.27}
$$

where we used the continuity of ψ and (3.11) in the second equality. Let us now turn to the second integral in the first line of (3.26)

$$
\begin{aligned}
&\int_{\mathbb{U}} \frac{\partial \psi}{\partial t} \nabla \cdot (\epsilon \nabla \psi) d\mathbf{x} = -\int_{\mathbb{U}} \epsilon \nabla \psi \nabla \frac{\partial \psi}{\partial t} d\mathbf{x} + \int_{\Gamma_t} \left[\epsilon \frac{\partial \psi}{\partial \mathbf{n}} \frac{\partial \psi}{\partial t} \right] dS \\
&= -\frac{d}{dt} \int_{\mathbb{U}} \frac{\epsilon}{2} |\nabla \psi|^2 d\mathbf{x} + \int_{\Omega_t} \frac{1}{2} \frac{\partial \epsilon}{\partial t} |\nabla \psi|^2 d\mathbf{x} + \int_{\Gamma_t} \left(\left[\frac{\epsilon}{2} |\nabla \psi|^2 \right] \mathbf{v}_1 \cdot \mathbf{n} + \left[\epsilon \frac{\partial \psi}{\partial \mathbf{n}} \frac{\partial \psi}{\partial t} \right] \right) dS \\
&= -\frac{d}{dt} \int_{\mathbb{U}} \frac{\epsilon}{2} |\nabla \psi|^2 d\mathbf{x} - \int_{\Omega_t} \frac{1}{2} \frac{d\epsilon}{d\phi_1} \nabla \cdot (\phi_1 \mathbf{v}_1) |\nabla \psi|^2 d\mathbf{x} \\
&\quad + \int_{\Gamma_t} \left(\left[\frac{\epsilon}{2} |\nabla \psi|^2 \right] \mathbf{v}_1 \cdot \mathbf{n} + \left[\epsilon \frac{\partial \psi}{\partial \mathbf{n}} \frac{\partial \psi}{\partial t} \right] \right) dS \\
&= -\frac{d}{dt} \int_{\mathbb{U}} \frac{\epsilon}{2} |\nabla \psi|^2 d\mathbf{x} - \int_{\Omega_t} (\phi_1 \mathbf{v}_1) \cdot \nabla p_{\Delta}^{\text{elec}} d\mathbf{x} \\
&\quad + \int_{\Gamma_t} \left(\left(\left[\frac{\epsilon}{2} |\nabla \psi|^2 \right] - \frac{1}{2} \phi_1 \frac{d\epsilon}{d\phi_1} |\nabla \psi|^2 \right) \mathbf{v}_1 \cdot \mathbf{n} + \left[\epsilon \frac{\partial \psi}{\partial \mathbf{n}} \frac{\partial \psi}{\partial t} \right] \right) dS
\end{aligned}
\tag{3.28}
$$

where we used (2.2) with $i = 1$ in the first equality and used (3.7) in the third equality. Substituting (3.27) and (3.27) into (3.26), we have:

$$
\begin{aligned}
&\frac{d}{dt}(E_{\text{ion}} + E_{\text{elec}}) + \int_{\Gamma_t} \left(\left(\left[\frac{\epsilon}{2} |\nabla \psi|^2 \right] - \frac{1}{2} \phi_1 \frac{d\epsilon}{d\phi_1} |\nabla \psi|^2 \right) \mathbf{v}_1 \cdot \mathbf{n} + \left[\epsilon \frac{\partial \psi}{\partial \mathbf{n}} \frac{\partial \psi}{\partial t} \right] \right) dS \\
&= - I_{\text{diff}} - P_{\text{elec}} - \int_{\Gamma_t} ((\mathcal{S}_g^{\text{elec}} - \mathcal{S}_{\text{f}}^{\text{elec}}) \mathbf{n}) \cdot \mathbf{v}_1 dS.
\end{aligned}
\tag{3.29}
$$

Using the definition of $\mathcal{S}_{g,f}^{\text{elec}}$ in (3.8), the above reduces to:

$$
\frac{d}{dt}(E_{\text{ion}} + E_{\text{elec}}) + \int_{\Gamma_t} \left[\epsilon \frac{\partial \psi}{\partial \mathbf{n}} \frac{\partial \psi}{\partial t} + ((\epsilon \nabla \psi \otimes \nabla \psi) \mathbf{n}) \cdot \mathbf{v}_1 \right] dS = -I_{\text{diff}} - P_{\text{elec}}. \tag{3.30}
$$

Let us examine the integrand in the above integral:

$$
\left[\epsilon \frac{\partial \psi}{\partial \mathbf{n}} \frac{\partial \psi}{\partial t} + ((\epsilon \nabla \psi \otimes \nabla \psi) \mathbf{n}) \cdot \mathbf{v}_1 \right] = \epsilon \frac{\partial \psi}{\partial \mathbf{n}} \left[\frac{\partial \psi}{\partial t} + \mathbf{v}_1 \cdot \nabla \psi \right], \tag{3.31}
$$

where we used (3.11). Note that the continuity of ψ across Γ_t (see (3.11)) implies that the jump on the right hand side must be 0 given that $\mathbf{v}_1$ coincides with the velocity of Γ_t. We have thus shown (3.17) and this concludes the proof. □

3.2 Electroneutral Limit

3.2.1 Electroneutral Model and the Energy Identity

To discuss the electroneutral limit, we first non-dimensionalize our system of equations. We first consider the scalar equations (2.2), (3.3)-(3.5). Introduce the primed dimensionless variables:

$$\begin{aligned} \mathbf{x} = L\mathbf{x}',\ \mathbf{v}_{1,2,f} = V_0\mathbf{v}'_{1,2,f},\ t = \frac{L}{V_0}t',\ D_k = D_0 D'_k, \\ c_k = c_0 c'_k,\ \psi = \frac{k_B T}{q}\psi',\ \rho_p = q c_0 \rho'_p,\ \epsilon = \epsilon_{\mathrm{f}}\epsilon', \end{aligned} \tag{3.32}$$

where L is the characteristic length (the size of the gel) and c_0, V_0 and D_0 are the representative ionic concentration, velocity and diffusion coefficient respectively. We shall prescribe V_0 in (3.40). The dielectric constant is scaled with respect to ϵ_{f}, the dielectric constant of the fluid. The scalar equations (2.1), (2.2), (3.3)-(3.5), in dimensionless form, are as follows:

$$\phi_1 + \phi_2 = 1,\ \ \frac{\partial \phi_i}{\partial t} + \nabla\cdot(\mathbf{v}_i\phi_i) = 0,\ \text{in } \Omega_t, \tag{3.33}$$

$$\frac{\partial(\phi_2 c_k)}{\partial t} + \nabla\cdot(\phi_2\mathbf{v}_2 c_k) = \mathrm{Pe}^{-1}\nabla\cdot\left(D_k\left(\nabla c_k + c_k z_k\nabla\psi\right)\right)\ \text{in } \Omega_t, \tag{3.34}$$

$$\frac{\partial c_k}{\partial t} + \nabla\cdot(\mathbf{v}_{\mathrm{f}} c_k) = \mathrm{Pe}^{-1}\nabla\cdot\left(D_k\left(\nabla c_k + c_k z_k\nabla\psi\right)\right)\ \text{in } \mathcal{R}_t, \tag{3.35}$$

$$-\beta^2\nabla\cdot(\epsilon\nabla\psi) = \begin{cases} \phi_1\rho_p + \sum_{k=1}^N z_k\phi_2 c_k & \text{in } \Omega_t \\ \sum_{k=1}^N z_k c_k & \text{in } \mathcal{R}_t \end{cases}, \tag{3.36}$$

Here and in the remainder of this Section, we drop the primes from the dimensionless variables unless noted otherwise. The dimensionless parameters are given by:

$$\mathrm{Pe} = \frac{V_0}{D_0/L},\ \beta = \frac{r_{\mathrm{d}}}{L},\ r_{\mathrm{d}} = \sqrt{\frac{\epsilon k_B T/q}{q c_0}}. \tag{3.37}$$

The parameter Pe is the Péclet number. The parameter β is the ratio between r_{d}, known as the Debye length, and the system size L. The Debye length is typically small compared to L, and therefore, it is of interest to consider the limit $\beta \to 0$. This is the electroneutral limit, to which we shall turn shortly.

The interface Γ_t moves according to (2.11), which can be made dimensionless by scaling v_Γ and $\mathbf{v}_1$ with respect to V_0. The interface conditions to (3.34)-(3.36) at Γ_t are given by the following dimensionless forms of (3.9), (3.10) and (3.11):

$$[\psi] = [\epsilon\nabla\psi \cdot \mathbf{n}] = [c_k] = 0, \tag{3.38}$$

$$((\mathbf{v}_\mathrm{f} - \mathbf{v}_1)c_k - D_k c_k \nabla\mu_k) \cdot \mathbf{n}|_{\mathcal{R}_t} = ((\mathbf{v}_2 - \mathbf{v}_1)\phi_2 c_k - D_k c_k \nabla\mu_k) \cdot \mathbf{n}|_{\Omega_t}, \tag{3.39}$$

where the chemical potential is now in dimensionless form: $\mu_k = \ln c_k + 1 + z_k\psi$.

We now make dimensionless the vector equations (2.4) and (2.8). Introduce the following primed dimensionless variables:

$$\begin{gathered}\kappa = \kappa_0\kappa',\ \eta_{1,2} = \eta_\mathrm{f}\eta'_{1,2},\ \eta_{\perp,\parallel} = \kappa_0 L\eta'_{\perp,\parallel},\ p = c_0 k_B T p', \\ p_\Delta^\mathrm{FH} = c_0 k_B T p_\Delta^{\mathrm{FH}\prime},\ \mathcal{T}_1^\mathrm{elas} = c_0 k_B T \mathcal{T}_1^{\mathrm{elas}\prime},\ \mathcal{S}_g^\mathrm{FH} = c_0 k_B T \mathcal{S}_g^{\mathrm{FH}\prime},\ V_0 = \frac{c_0 k_B T}{\kappa_0 L},\end{gathered} \tag{3.40}$$

where κ_0 is the representative magnitude of the friction coefficient. We have used the characteristic pressure $c_0 k_B T$ and κ_0 to prescribe the characteristic velocity V_0. Equations (2.4) and (2.8) now take the following dimensionless form:

$$\begin{aligned}\nabla \cdot \mathcal{T}_1^\mathrm{elas} + \zeta\nabla \cdot (\eta_1(\nabla\mathbf{v}_1 + (\nabla\mathbf{v}_1)^T)) - \phi_1\nabla(p + p_\Delta^\mathrm{FH}) - \kappa(\mathbf{v}_1 - \mathbf{v}_2)& \\ = \phi_1\rho_p\nabla\psi - \beta^2\phi_1\nabla\left(\frac{1}{2}\frac{d\epsilon}{d\phi_1}|\nabla\psi|^2\right) \text{ in } \Omega_t&\end{aligned} \tag{3.41}$$

$$\zeta\nabla \cdot (\eta_2(\nabla\mathbf{v}_2 + (\nabla\mathbf{v}_2)^T)) - \phi_2\nabla p - \kappa(\mathbf{v}_2 - \mathbf{v}_1) = \sum_{k=1}^N z_k\phi_2 c_k\nabla\psi, \text{ in } \Omega_t, \tag{3.42}$$

$$\zeta\nabla \cdot (\nabla\mathbf{v}_\mathrm{f} + (\nabla\mathbf{v}_\mathrm{f})^T) - \nabla p = \sum_{k=1}^N z_k c_k\nabla\psi, \text{ in } \mathcal{R}_t, \tag{3.43}$$

The inertial terms have been dropped for simplicity. Expressions (2.41), (3.6) and (3.7) were used as expressions for $\mathbf{f}_2, \mathbf{g}_2, \mathbf{f}_\mathrm{f}$ and p_Δ. The dimensionless variable $\zeta = \eta_\mathrm{f}/(\kappa_0 L^2)$ is the ratio between the characteristic viscous and frictional forces.

The interface conditions at Γ_t for (3.41)-(3.43) are given by (2.12), (2.13), (2.16), (2.44) and (2.45) in dimensionless form. Equations (2.12), (2.13) and (2.45) can be made dimensionless by rescaling the velocities w and $\mathbf{q}$ (as well as $\mathbf{v}_{1,2,\mathrm{f}}$) are with respect to V_0 so that $w = V_0 w'$ and $\mathbf{q} = V_0\mathbf{q}'$. Equations (2.16) and (2.44) take the following form:

$$\left(\zeta(\nabla\mathbf{v}_\mathrm{f} + (\nabla\mathbf{v}_\mathrm{f})^T) + \beta^2\left(\nabla\psi\otimes\nabla\psi - \frac{1}{2}|\nabla\psi|^2 I\right)\right)\mathbf{n} - p|_{\mathcal{R}_t}\mathbf{n}$$

$$
\begin{aligned}
&= \left(\mathcal{T}_1^{\mathrm{elas}} + \mathcal{S}_g^{\mathrm{FH}} + \zeta\eta_1(\nabla\mathbf{v}_1 + (\nabla\mathbf{v}_1)^T) + \zeta\eta_2(\nabla\mathbf{v}_2 + (\nabla\mathbf{v}_2)^T)\right)\mathbf{n} - p|_{\Omega_t}\mathbf{n} \\
&\quad + \beta^2\left(\epsilon\nabla\psi\otimes\nabla\psi - \frac{1}{2}\left(\epsilon - \phi_1\frac{d\epsilon}{d\phi_1}\right)|\nabla\psi|^2 I\right)\mathbf{n}, \qquad (3.44)
\end{aligned}
$$

$$
\begin{aligned}
\eta_\perp w &= \Pi_\perp, \\
\Pi_\perp &= [p] - \mathbf{n}\cdot\left(\zeta\frac{\eta_2}{\phi_2}(\nabla\mathbf{v}_2 + (\nabla\mathbf{v}_2)^T)\right)\mathbf{n} + \mathbf{n}\cdot\zeta\left(\nabla\mathbf{v}_{\mathrm{f}} + (\nabla\mathbf{v}_{\mathrm{f}})^T\right)\mathbf{n}. \qquad (3.45)
\end{aligned}
$$

The boundary condition in the outer boundary of $\mathbb{U}$ are given by (2.18), (3.12) and (3.13) in dimensionless form.

In many cases of practical interest, the Debye length r_{d} is small compared to the system size. We thus consider the limit $\beta \to 0$, while keeping the other dimensionless constants fixed. Let us consider the Poisson equation (3.36). Setting $\beta = 0$, we obtain the following electroneutrality condition:

$$
\begin{aligned}
\phi_1\rho_p + \sum_{k=1}^N z_k\phi_2 c_k &= 0 \text{ in } \Omega_t, \\
\sum_{k=1}^N z_k c_k &= 0 \text{ in } \mathcal{R}_t.
\end{aligned} \qquad (3.46)
$$

If we replace the Poisson equation by the above algebraic constraints, boundary conditions (3.11) (or the boundary conditions for ψ in (3.38)) or (3.13) can no longer be satsified. This indicates that, as $\beta \to 0$, a boundary layer whose thickness is of order β (or r_{d} in dimensional terms) develops at the interface Γ_t, within which electroneutrality is violated. This is known as the Debye layer [32]. (A Debye layer does not develop at $\partial\mathbb{U}$ given our choice of imposing no-flux boundary conditions for ψ.) Thus, in deriving the equations to be satisfied in the limit $\beta \to 0$, care must be taken to capture effects arising from the Debye layer. We refer to the resulting system as the *electroneutral model*. The system before taking this limit will be referred to as the *Poisson model*. In the rest of this Section, we shall state the equations and boundary condtions of electroneutral model, and establish the free energy identity satisfied by the model. In Section 3.2.2, we shall use matched asymptotic analysis at the Debye layer to derive the electroneutral model in the limit $\beta \to 0$.

Let us now describe the electroneutral model. As stated above, we replace (3.36) with the electroneutrality conditions (3.46). The electrostatic potential ψ evolves so that the electroneutrality constraint is satisfied everywhere at each time instant.

Given the electroneutrality condition, the right hand side of (3.43), is now 0. All other bulk equations remain the same.

We turn to boundary conditions. We no longer have boundary conditions for ψ ((3.11) or (3.13)), as discussed above. Consider the boundary conditions for the ionic concentrations c_k. We continue to require the flux conditions (3.39) at Γ_t and (3.12) at $\partial\mathbb{U}$. We must, however, abandon condition (3.38), that c_k be continuous across Γ_t. If all the c_k were continuous across Γ_t, the electroneutrality condition (3.46) would imply that $\phi_2\rho_p$ must be 0. This cannot hold in general. Instead of continuity of c_k, we require continuity of the chemical potential μ_k across Γ_t:

$$[\mu_k] = 0, \; k = 1, \cdots, N. \tag{3.47}$$

This is a standard condition imposed when the electroneutral approximation is used [32]. We shall discuss this condition in Section 3.2.2.

Let us turn to the boundary conditions for the vector equations. Boundary conditions (2.12), (2.13) and (2.45) at Γ_t remain the same, and we continue to require (2.18) at $\partial\mathbb{U}$. For boundary condition (3.44), we simply set $\beta = 0$, thereby eliminating stresses of electrostatic origin. The non-trivial modification concerns the boundary condition (3.45). We let:

$$\begin{aligned} &\eta_\perp w = \widehat{\Pi_\perp}, \; \widehat{\Pi_\perp} = \Pi_\perp - \pi_{\text{osm}}, \\ &\pi_{\text{osm}} = \left[\sum_{k=1}^N c_k \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} - \mathcal{W}_{\text{ion}}\right] = \sum_{k=1}^N [c_k]. \end{aligned} \tag{3.48}$$

where $\mathcal{W}_{\text{ion}}$ defined in (3.1) has been made dimensionless by scaling with respect to k_BT. In physical dimensions, π_{osm} takes the form:

$$\pi_{\text{osm}} = k_BT \sum_{k=1}^N [c_k]. \tag{3.49}$$

This is nothing other than the familiar van't Hoff expression for osmotic pressure. Equation (3.48) thus states that water flow across the interface Γ_t is driven by the mechanical force difference as well as the osmotic pressure difference across Γ_t. We shall derive this condition using matched asymptotics in Section 3.2.2.

The electroneutral model described above satisfies the following energy identity.

Theorem 3.2. *Let ϕ_i, c_k and ψ be smooth functions satisfying* (3.33)-(3.35), (3.46), *with boundary conditions* (3.47), (3.39), *and* (3.12) *(in dimensionless form). Let* $\mathbf{v}_i$ *and* $\mathbf{v}_{\mathrm{f}}$ *be smooth functions satisfying* (3.41) *with* $\beta = 0$, (3.42) *and* (3.43). *For boundary conditions, we require* (3.44) *with* $\beta = 0$ *and* (3.48) *as well as* (2.12), (2.13), (2.45) *and* (2.18) *(in dimensionless form). Then, the following identity holds:*

$$\frac{d}{dt}(E_{\mathrm{elas}} + E_{\mathrm{FH}} + E_{\mathrm{ion}}) = -I_{\mathrm{visc}} - I_{\mathrm{diff}} - J_{\mathrm{visc}}, \tag{3.50}$$

where $E_{\mathrm{elas}}, E_{\mathrm{FH}}, I_{\mathrm{visc}}, J_{\mathrm{visc}}, E_{\mathrm{ion}}$ *and* I_{diff} *are the suitably non-dimensionalized versions of the quantities defined in* (2.48) *and* (3.15).

We note that the above statement remains true if we retain the inertial terms in (3.41)-(3.43), (3.44) and (3.48) as long as we include the kinetic energy dE_{KE}/dt in the left hand side of (3.50).

Proof. The proof is completely analogous to Theorem 3.1. Expressions (3.24) and (3.25) also hold in the electroneutral case. Let us now add (3.24) and (3.25). We find:

$$\frac{d}{dt}E_{\mathrm{ion}} = \int_{\Gamma_t} \pi_{\mathrm{osm}} w dS - I_{\mathrm{diff}} - P_{\mathrm{elec}} \tag{3.51}$$

where we used (3.46), (3.47), and the definition of π_{osm} in (3.48). Now, Theorem 2.1 yields:

$$\frac{d}{dt}(E_{\mathrm{elas}} + E_{\mathrm{FH}}) = -\int_{\Gamma_t} \left(\Pi_\perp w + \eta_\parallel |\mathbf{q}|^2\right) dS - I_{\mathrm{visc}} + P_{\mathrm{elec}}. \tag{3.52}$$

The integral on the right hand side of the above is *not* equal to J_{visc} as defined in (2.48) since we have now adopted (3.48) instead of (2.44) as our boundary condition for w. Now, adding (3.51) and (3.52) and using (3.48), we obtain (3.50). □

The reader of the above proof will realize that (3.47) and (3.48) are the only conditions that will allow an energy dissipation relation of the type (3.50) to hold. It may be said that, in the limit as $\beta \to 0$, boundary conditions (3.47) and (3.48) are forced upon us by the requirement that the limiting system satisfy a free energy identity. It is interesting that we do indeed recover the classical van't Hoff expression for osmotic pressure if we adopt (3.1) as our expression for $\mathcal{W}_{\mathrm{ion}}$. We also point out that the conditions for stationary state for the above equations reduce to the Donnan conditions first proposed in [30]. In this sense, our electroneutral model is a dynamic extension of the static calculations in [30].

3.2.2 Matched Asymtotic Analysis

We have seen above that boundary conditions (3.47) and (3.48) arise naturally from the requirement of free energy dissipation. The goal of this Section is to derive the limiting boundary conditions (3.47) and (3.48) by way of matched asymptotic analysis.

Consider a family of solutions for the Poisson model with the same initial condition but with different values of $\beta > 0$. We let the initial condition satisfy the electroneutrality condition. Suppose, for sufficiently small values of β, a smooth solution to this initial value problem exists for positive time. We study the behavior of this family of solutions as $\beta \to 0$.

Given the presence of the boundary layer at Γ_t, we introduce a curvilinear coordinate system that conforms to and advects with Γ_t. Our first step is to rewrite the dimensionless Poisson model in this coordinate system using tensor calculus (see, for example, [33] or [34] for a treatment of tensor calculus in the context of continuum mechanics).

Introduce a local coordinate system $\mathbf{y}_\Gamma = (y^1, y^2)$ on the initial surface Γ_0 so that $\mathbf{x}_\Gamma(\mathbf{y}_\Gamma, 0)$ gives the $\mathbf{x}$-coordinates of the surface Γ_0. Advect this coordinate system with the polymer velocity $\mathbf{v}_1$:

$$\frac{\partial \mathbf{x}_\Gamma}{\partial t} = \mathbf{v}_1. \tag{3.53}$$

The solution to the above equation gives a local coordinate system $\mathbf{x}_\Gamma(\mathbf{y}_\Gamma, t)$ on Γ_t for positive time. The coordinate $\mathbf{y}_\Gamma$ may be seen as the material coordinate system of the polymer phase restricted to the gel-fluid interface Γ_t.

Define the signed distance function:

$$y^3(\mathbf{x}, t) = \begin{cases} -\text{dist}(\mathbf{x}, \Gamma_t) & \text{if } \mathbf{x} \in \Omega_t, \\ \text{dist}(\mathbf{x}, \Gamma_t) & \text{if } \mathbf{x} \in \mathcal{R}_t. \end{cases} \tag{3.54}$$

By taking a smaller intial coordinate patch if necessary, $\mathbf{y} = (\mathbf{y}_\Gamma, y^3) = (y^1, y^2, y^3)$ can be made into a coordinate system (in $\mathbb{R}^3$) near $\mathbf{x} = \mathbf{x}_\Gamma(\mathbf{0}, t)$ for $t \geq 0$ We denote this coordinate map by $\mathcal{C}_t$ as follows:

$$\mathbf{x} = \mathcal{C}_t(\mathbf{y}), \text{ for } \mathbf{y} \in \mathcal{N} \subset \mathbb{R}^3 \tag{3.55}$$

where $\mathcal{N}$ is the open neighborhood on which the coordinate map is defined.

We shall need the following quantities pertaining to the $\mathbf{y}$ coordinate system. Define the metric tensor $g_{\sigma\tau}$ associated with the $\mathbf{y}$ coordinate system:

$$g_{\sigma\tau} = \frac{\partial \mathcal{C}_t}{\partial y^\sigma} \cdot \frac{\partial \mathcal{C}_t}{\partial y^\tau},\ \sigma, \tau = 1, 2, 3. \tag{3.56}$$

where $\cdot$ denotes the standard inner product in $\mathbb{R}^3$. We let $g^{\sigma\tau}$ be the inverse $g_{\sigma\tau}$ in the sense that:

$$g^{\sigma\alpha} g_{\alpha\tau} = \delta^\sigma_\tau \tag{3.57}$$

where δ^σ_τ is the Kronecker delta. In the above and henceforth, the summation convention is in effect for repeated Greek indices. Given (3.54), we have:

$$g_{33} = g^{33} = 1,\ g_{\sigma 3} = g_{3\sigma} = g^{\sigma 3} = g^{\sigma 3} = 0 \text{ for } \sigma = 1, 2. \tag{3.58}$$

Define the Christoffel symbols associated with $g_{\sigma\tau}$ as follows:

$$\Gamma^\alpha_{\sigma\tau} = \frac{1}{2} g^{\alpha\gamma} \left(\frac{\partial g_{\sigma\gamma}}{\partial y^\tau} + \frac{\partial g_{\tau\gamma}}{\partial y^\sigma} - \frac{\partial g_{\sigma\tau}}{\partial y^\gamma} \right). \tag{3.59}$$

From (3.58), it can be seen after some calculation that:

$$\Gamma^3_{3\sigma} = 0 \text{ for } \sigma = 1, 2, 3. \tag{3.60}$$

Let $\hat{\mathbf{v}}$ be the velocity field of the points with fixed $\mathbf{y}$ coordinate:

$$\hat{\mathbf{v}} = \frac{\partial \mathcal{C}_t}{\partial t}. \tag{3.61}$$

We shall use the fact that:

$$\hat{\mathbf{v}}(\mathbf{y}_\Gamma, y_3 = 0) = \mathbf{v}_1, \tag{3.62}$$

which is just a restatement of (3.53). Finally, we assume the following condition on $g_{\sigma\tau}$:

$$g_{\sigma\tau}, g^{\sigma\tau}, \frac{\partial}{\partial y^\alpha} g_{\sigma\tau} \text{ remain bounded as } \beta \to 0. \tag{3.63}$$

This condition ensures that the surface Γ_t does not become increasingly ill-behaved as $\beta \to 0$, and ensures the presence of a boundary layer as $\beta \to 0$. In particular, this condition allows one to choose $\mathcal{N}$ in (3.55) independent of β.

We rewrite equations (3.33)-(3.43) in the coordinate system $(\mathbf{y}, t)$ instead of $(\mathbf{x}, t)$.

Note that expressions involving the vector variables $\mathbf{v} = \mathbf{v}_{1,2,f}$ or $\hat{\mathbf{v}}$ must be rewritten in terms of (v^1, v^2, v^3), the $\mathbf{y}$-components of the vector field, defined as follows:

$$\mathbf{v} = v^1 \frac{\partial \mathcal{C}_t}{\partial y^1} + v^2 \frac{\partial \mathcal{C}_t}{\partial y^2} + v^3 \frac{\partial \mathcal{C}_t}{\partial y^3}. \tag{3.64}$$

Let us first rewrite the scalar equations (3.33)-(3.36).

$$\phi_1 + \phi_2 = 1, \ \frac{\partial \phi_i}{\partial t} - \hat{v}^\sigma \mathcal{D}_\sigma \phi_i + \mathcal{D}_\sigma(\phi_i v_i^\sigma) = 0, \text{ for } y^3 < 0 \tag{3.65}$$

$$\begin{aligned} &\frac{\partial(\phi_2 c_k)}{\partial t} - \hat{v}^\sigma \mathcal{D}_\sigma(\phi_2 c_k) + \mathcal{D}_\sigma(\phi_2 c_k v_2^\sigma) \\ &\qquad = \mathrm{Pe}^{-1} g^{\sigma\tau} \mathcal{D}_\sigma(D_k(\mathcal{D}_\tau c_k + c_k z_k \mathcal{D}_\tau \psi)) \text{ for } y^3 < 0 \end{aligned} \tag{3.66}$$

$$\frac{\partial c_k}{\partial t} - \hat{v}^\sigma \mathcal{D}_\sigma c_k + \mathcal{D}_\sigma(c_k v_{\mathrm{f}}^\sigma) = \mathrm{Pe}^{-1} g^{\sigma\tau} \mathcal{D}_\sigma(D_k(\mathcal{D}_\tau c_k + c_k z_k \mathcal{D}_\tau \psi)) \text{ for } y^3 > 0 \tag{3.67}$$

$$-\beta^2 g^{\sigma\tau} \mathcal{D}_\sigma(\epsilon \mathcal{D}_\tau \psi) = \begin{cases} \phi_1 \rho_p + \sum_{k=1}^N z_k \phi_2 c_k & \text{for } y^3 < 0 \\ \sum_{k=1}^N z_k c_k & \text{for } y^3 > 0 \end{cases} \tag{3.68}$$

In the above, $\mathcal{D}_\sigma$ is the covariant derivative with respect to y^σ. The function v_Γ is the magnitude of $\mathbf{v}_\Gamma$ defined in (3.61). We shall need the boundary conditions (3.38):

$$\psi|_{y^3=0+} = \psi|_{y^3=0-}, \ c_k|_{y^3=0+} = c_k|_{y^3=0-}, \ \epsilon \frac{\partial \psi}{\partial y^3}\bigg|_{y^3=0+} = \epsilon \frac{\partial \psi}{\partial y^3}\bigg|_{y^3=0-} \tag{3.69}$$

where $\cdot|_{y^3=\pm 0}$ denotes the limiting value as $y^3 = 0$ is approached from above or below.

We shall only need the vector equations for $\mathbf{v}_2$ and $\mathbf{v}_{\mathrm{f}}$. Equations (3.42) and (3.43) are rewritten as follows:

$$\begin{aligned} &\zeta(g^{\sigma\tau} \mathcal{D}_\sigma(\eta_2(\mathcal{D}_\tau v_2^\alpha)) + g^{\alpha\tau} \mathcal{D}_\sigma(\eta_2(\mathcal{D}_\tau v_2^\sigma))) - \phi_2 g^{\alpha\sigma} \mathcal{D}_\sigma p \\ &\qquad = \kappa(v_2^\alpha - v_1^\alpha) + \sum_{k=1}^N z_k \phi_2 c_k g^{\alpha\sigma} \mathcal{D}_\sigma \psi, \text{ for } y^3 < 0, \end{aligned} \tag{3.70}$$

$$\begin{aligned} &\zeta(g^{\sigma\tau} \mathcal{D}_\sigma(\mathcal{D}_\tau v_{\mathrm{f}}^\alpha) + g^{\alpha\tau} \mathcal{D}_\sigma(\mathcal{D}_\tau v_{\mathrm{f}}^\sigma)) - \phi_2 g^{\alpha\sigma} \mathcal{D}_\sigma p \\ &\qquad = \sum_{k=1}^N z_k c_k g^{\alpha\sigma} \mathcal{D}_\sigma \psi, \text{ for } y^3 > 0. \end{aligned} \tag{3.71}$$

We shall need boundary condition (3.45):

$$\eta_\perp w = p|_{y^3=0-} - p|_{y^3=0+} - 2\zeta\frac{\eta_2}{\phi_2}\frac{\partial v_2^3}{\partial y^3} + 2\zeta\frac{\partial v_{\mathrm{f}}^3}{\partial y^3}. \tag{3.72}$$

We introduce an inner layer coordinate system $\mathbf{Y} = (\mathbf{y}_\Gamma, \xi)$ where $y_3 = \beta\xi$. We adopt the ansatz that all physical quantities have an expansion in terms of β. For example:

$$c_k = c_k^0 + \beta c_k^1 + \cdots\ ,\ v_1^\alpha = v_1^{\alpha,0} + \beta v_1^{\alpha,1} + \cdots\ , \tag{3.73}$$

and likewise for other physical variables.

The Equilibrium Case

Suppose the system approaches a stationary state as $t \to \infty$. We first perform our calculations for the stationary solutions. Our derivation here assumes the existence of solutions to the inner and outer layer equations satisfying the standard matching conditions.

At the stationary state, all time derivatives are 0 and thus, the right hand side of the energy identity in (3.15) must be 0. From the condition that $I_{\mathrm{diff}} = 0$, we see that $\nabla\mu_k = 0$. Given the continuity of c_k and ψ across Γ_t, we have:

$$\mu_k \text{ is constant throughout } \mathbb{U}. \tag{3.74}$$

This condition should persist in the limit $\beta \to 0$, and we have thus derived (3.47).

To derive (3.48), we first show that all velocities are identically equal to 0. Given $I_{\mathrm{visc}} = J_{\mathrm{visc}} = 0$ and using the definitions of w and $\mathbf{q}$ in J_{visc}, we have (see (2.48),(2.12) and (2.13)):

$$\nabla_S \mathbf{v}_{\mathrm{f}} = 0 \text{ in } \mathcal{R}_t,\ \nabla_S \mathbf{v}_2 = 0, \mathbf{v}_1 = \mathbf{v}_2 \text{ in } \Omega_t, \tag{3.75}$$

$$\mathbf{v}_2 = \mathbf{v}_{\mathrm{f}} \text{ on } \Gamma_t. \tag{3.76}$$

The vanishing of the symmetric gradient implies that $\mathbf{v}_{\mathrm{f}}$ and $\mathbf{v}_2$ are velocity fields representing rigid rotation and translation. Given that $\mathbf{v}_{\mathrm{f}} = 0$ on $\partial\mathbb{U}$, we have $\mathbf{v}_{\mathrm{f}} = 0$ throughout $\mathcal{R}_t$. From (3.76), we see that $\mathbf{v}_2 = 0$ on $\Gamma_t = \partial\Omega_t$, and we thus have $\mathbf{v}_2 = 0$ throughout Ω_t. From (3.75), we see that $\mathbf{v}_1 = \mathbf{v}_2 = 0$ in Ω_t.

We now examine equations (3.70) and (3.71). Given that all velocities are equal to 0, the leading order equations are:

$$-\frac{\partial p^0}{\partial \xi} = \sum_{k=1}^{N} z_k c_k^0 \frac{\partial \psi^0}{\partial \xi}, \text{ for } \xi < 0 \text{ and } \xi > 0. \tag{3.77}$$

The boundary conditions that we need at $\xi = 0$ to leading order are (see (3.69) and (3.72)):

$$\lim_{\xi \to 0-} c_k^0 = \lim_{\xi \to 0+} c_k^0, \; \lim_{\xi \to 0-} \psi^0 = \lim_{\xi \to 0+} \psi^0, \; \lim_{\xi \to 0-} p^0 = \lim_{\xi \to 0+} p^0. \tag{3.78}$$

The matching conditions for the leading order terms are:

$$\begin{aligned}
\lim_{\xi \to \pm\infty} c_k^0(\mathbf{y}_\Gamma, \xi) &= \lim_{y^3 \to 0\pm} c_k^0(\mathbf{y}_\Gamma, y^3) \equiv c_{k,\pm}^0, \\
\lim_{\xi \to \pm\infty} \psi^0(\mathbf{y}_\Gamma, \xi) &= \lim_{y^3 \to 0\pm} \psi^0(\mathbf{y}_\Gamma, y^3) \equiv \psi_\pm^0, \\
\lim_{\xi \to \pm\infty} p^0(\mathbf{y}_\Gamma, \xi) &= \lim_{y^3 \to 0\pm} p^0(\mathbf{y}_\Gamma, y^3) \equiv p_\pm^0
\end{aligned} \tag{3.79}$$

Note that, given (3.74), we have:

$$\frac{\partial c_k^0}{\partial \xi} + z_k c_k^0 \frac{\partial \psi^0}{\partial \xi} = 0 \text{ for } \xi < 0 \text{ and } \xi > 0. \tag{3.80}$$

Integrating (3.77) from $\xi = -\infty$ to ∞, we have:

$$\begin{aligned}
p_+^0 - p_-^0 &= \int_{-\infty}^{\infty} \frac{\partial p^0}{\partial \xi} d\xi = -\sum_{k=1}^{N} \int_{-\infty}^{\infty} z_k c_k^0 \frac{\partial \psi^0}{\partial \xi} d\xi \\
&= \sum_{k=1}^{N} \int_{-\infty}^{\infty} \frac{\partial c_k^0}{\partial \xi} d\xi = \sum_{k=1}^{N} (c_{k,-}^0 - c_{k,+}^0).
\end{aligned} \tag{3.81}$$

where we have used (3.78) and (3.79) in the first equality, (3.77) in the second equality, (3.80) in the third equality and (3.86) and (3.79) in the last equality. The above expression is nothing other than (3.48) where the velocities are taken to be 0.

The Dynamic Case

The dynamic case is somewhat more involved, but the essence of the derivation remains the same as in the equilibrium case. We shall derive (3.47) and (3.48) at points on Γ_t such that the water flow w does not vanish to leading order. This condition can equivalently be written as:

$$v_1^{3,0} \neq v_2^{3,0}. \tag{3.82}$$

As in the equilibrium case, we assume the existence of solutions to the inner and outer layer equations satisfying the standard matching conditions.

We first derive (3.47). Explicitly write out the covariant derivatives in (3.67):

$$\begin{aligned}
&\frac{\partial c_k}{\partial t} - \hat{v}^\sigma \frac{\partial c_k}{\partial y^\sigma} + \frac{\partial (c_k v_{\mathrm{f}}^\sigma)}{\partial y^\sigma} + \Gamma^\sigma_{\sigma\tau} c_k v_{\mathrm{f}}^\tau \\
=&\mathrm{Pe}^{-1} g^{\sigma\tau}\left(\frac{\partial}{\partial y^\sigma}\left(D_k \frac{\partial c_k}{\partial y^\tau} + c_k z_k \frac{\partial \psi}{\partial y^\tau}\right) - \Gamma^\alpha_{\sigma\tau}\left(D_k \frac{\partial c_k}{\partial y^\alpha} + c_k z_k \frac{\partial \psi}{\partial y^\alpha}\right)\right).
\end{aligned} \tag{3.83}$$

We now rescale y^3 to $\beta\xi$ to obtain the leading orde equation in the inner layer. Given our assumption (3.63), the terms involving the Christoffel symbols $\Gamma^\alpha_{\sigma\tau}$ do not make contributions to leading order. Using (3.58), we have, to leading order:

$$0 = \frac{\partial}{\partial \xi}\left(D_k\left(\frac{\partial c_k^0}{\partial \xi} + z_k c_k^0 \frac{\partial \psi^0}{\partial \xi}\right)\right) \text{ for } \xi > 0. \tag{3.84}$$

We may perform a similar calculation for (3.66) to obtain:

$$0 = \frac{\partial}{\partial \xi}\left(D_k\left(\frac{\partial c_k^0}{\partial \xi} + z_k c_k^0 \frac{\partial \psi^0}{\partial \xi}\right)\right) \text{ for } \xi < 0. \tag{3.85}$$

Note that the diffusion coefficient may be spatially non-constant for $\xi < 0$ since D_k is in general a function of ϕ_2. The boundary conditions that we need at $\xi = 0$ to leading order are (see (3.69)):

$$\lim_{\xi\to 0-} c_k^0 = \lim_{\xi\to 0+} c_k^0, \; \lim_{\xi\to 0-} \psi^0 = \lim_{\xi\to 0+} \psi^0. \tag{3.86}$$

The matching conditions for the leading order terms are:

$$\begin{aligned}
\lim_{\xi\to\pm\infty} c_k^0(\mathbf{y}_\Gamma, \xi, t) &= \lim_{y^3\to 0\pm} c_k^0(\mathbf{y}_\Gamma, y^3, t) \equiv c_{k,\pm}^0, \\
\lim_{\xi\to\pm\infty} \psi^0(\mathbf{y}_\Gamma, \xi, t) &= \lim_{y^3\to 0\pm} \psi^0(\mathbf{y}_\Gamma, y^3, t) \equiv \psi_\pm^0,
\end{aligned} \tag{3.87}$$

This suggests that the ξ derivatives of c_k^0 and ψ^0 should tend to 0 as $\xi \to \pm\infty$.

Therefore, from (3.84) and (3.85) we have:

$$\frac{\partial c_k^0}{\partial \xi} + z_k c_k^0 \frac{\partial \psi^0}{\partial \xi} = 0, \tag{3.88}$$

where we have used the fact that $D_k > 0$ and assumed that D_k remains bounded over the inner layer. Let $\mu_k^0 = \ln c_k^0 + \psi^0$. We have:

$$\begin{aligned}
&\lim_{y^3 \to 0-} \mu_k^0(\mathbf{y}_\Gamma, y^3, t) - \lim_{y^3 \to 0+} \mu_k^0(\mathbf{y}_\Gamma, y^3, t) \\
&= \lim_{\xi \to -\infty} \mu_k^0(\mathbf{y}_\Gamma, \xi, t) - \lim_{\xi \to \infty} \mu_k^0(\mathbf{y}_\Gamma, \xi, t) \\
&= -\int_{-\infty}^{\infty} \left(\frac{1}{c_k^0} \frac{\partial c_k^0}{\partial \xi} + z_k \frac{\partial \psi^0}{\partial \xi} \right) d\xi = 0.
\end{aligned} \tag{3.89}$$

where we used the matching conditions (3.87) in the first equality and (3.86) in the second equality, and (3.88) in the last equality. We have thus derived (3.47).

We now turn to the derivation of (3.48). We first show that $v_1^{3,0}, v_2^{3,0}, v_{\mathrm{f}}^{3,0}, \phi_i^0$ are all independent of ξ in the inner layer. Equation (3.71) may be written explicitly as:

$$\begin{aligned}
&\zeta g^{\sigma\tau} \left(\frac{\partial}{\partial y^\sigma} \left(\frac{\partial v_{\mathrm{f}}^\alpha}{\partial y^\tau} + \Gamma^\alpha_{\tau\gamma} v^\gamma \right) + \Gamma^\alpha_{\sigma\delta} \left(\frac{\partial v_{\mathrm{f}}^\delta}{\partial y^\tau} + \Gamma^\delta_{\tau\gamma} v^\gamma \right) - \Gamma^\delta_{\sigma\tau} \left(\frac{\partial v_{\mathrm{f}}^\alpha}{\partial y^\delta} + \Gamma^\alpha_{\delta\gamma} v^\gamma \right) \right) \\
&+\zeta g^{\alpha\tau} \left(\frac{\partial}{\partial y^\sigma} \left(\frac{\partial v_{\mathrm{f}}^\sigma}{\partial y^\tau} + \Gamma^\sigma_{\tau\gamma} v^\gamma \right) + \Gamma^\sigma_{\sigma\delta} \left(\frac{\partial v_{\mathrm{f}}^\delta}{\partial y^\tau} + \Gamma^\delta_{\tau\gamma} v^\gamma \right) - \Gamma^\delta_{\sigma\tau} \left(\frac{\partial v_{\mathrm{f}}^\sigma}{\partial y^\delta} + \Gamma^\sigma_{\delta\gamma} v^\gamma \right) \right) \\
&-\phi_2 g^{\alpha\sigma} \frac{\partial p}{\partial y^\sigma} = \sum_{k=1}^N z_k c_k g^{\alpha\sigma} \frac{\partial \psi}{\partial y^\sigma}.
\end{aligned} \tag{3.90}$$

Given (3.63), the terms involving Christoffel symbols do not contribute to leading order in the inner layer. Using (3.58), we obtain:

$$\frac{\partial}{\partial \xi} \left(\frac{\partial v_{\mathrm{f}}^{\alpha,0}}{\partial \xi} \right) = 0 \text{ for } \xi > 0. \tag{3.91}$$

A similar calculation for (3.70) yields:

$$\frac{\partial}{\partial \xi} \left(\eta_2 \frac{\partial v_2^{\alpha,0}}{\partial \xi} \right) = 0 \text{ for } \xi < 0. \tag{3.92}$$

The matching conditons are:

$$\begin{aligned}\lim_{\xi\to-\infty} v_2^{\alpha,0}(\mathbf{y}_\Gamma,\xi,t) &= \lim_{y^3\to 0-} v_2^{\alpha,0}(\mathbf{y}_\Gamma,y^3,t) \equiv v_{2,-}^{\alpha,0},\\ \lim_{\xi\to\infty} v_{\mathrm{f}}^{\alpha,0}(\mathbf{y}_\Gamma,\xi,t) &= \lim_{y^3\to 0+} v_{\mathrm{f}}^{\alpha,0}(\mathbf{y}_\Gamma,y^3,t) \equiv v_{\mathrm{f},+}^{\alpha,0}.\end{aligned} \tag{3.93}$$

From this and the assumption that $\eta_2 > 0$ stays bounded, we conclude that $v_2^{\alpha,0}$ and $v_{\mathrm{f}}^{\alpha,0}$ do not depend on ξ and that:

$$v_2^{\alpha,0}(\mathbf{y}_\Gamma,\xi,t) = v_{2,-}^{\alpha,0}(\mathbf{y}_\Gamma,t),\ v_{\mathrm{f}}^{\alpha,0}(\mathbf{y}_\Gamma,\xi,t) = v_{\mathrm{f},+}^{\alpha,0}(\mathbf{y}_\Gamma,t). \tag{3.94}$$

Consider the equation for ϕ_2 in (3.65). To leading order in the inner layer, we have, using (3.63):

$$-\hat{v}^{3,0}\frac{\partial\phi_2^0}{\partial\xi} + \frac{\partial(v_2^{3,0}\phi_2^0)}{\partial\xi} = 0. \tag{3.95}$$

Given the definition of $\hat{\mathbf{v}}$ and (3.62), we have:

$$\hat{v}^{3,0} = v_1^{3,0}\big|_{\xi=0-}. \tag{3.96}$$

Using this and (3.94), (3.95) becomes:

$$\left(-\, v_1^{3,0}\big|_{\xi=0-} + v_2^{3,0}\big|_{\xi=0-}\right)\frac{\partial\phi_2^0}{\partial\xi} = 0. \tag{3.97}$$

By assumption (3.82), we conclude that ϕ_2^0 does not depend on ξ. Given $\phi_1^0+\phi_2^0 = 1$ from (3.65), we see that ϕ_1^0 is also independent of ξ. Using the usual matching conditions, we thus have:

$$\phi_i^0(\mathbf{y}_\Gamma,\xi,t) = \lim_{y_3\to 0-}\phi_i^0(\mathbf{y}_\Gamma,y^3,t) \equiv \phi_{i,-}^0. \tag{3.98}$$

To show that $v_1^{3,0}$ does not depend on ξ, consider the following expression:

$$\sum_{i=1}^{2}\mathcal{D}_\sigma(\phi_i v_i^\sigma) = 0, \tag{3.99}$$

which can be obtained by summing the equations for ϕ_i in (3.65) for $i = 1, 2$. To leading order, using (3.63), this equation yields:

$$\frac{\partial}{\partial \xi}(\phi_1^0 v_1^{3,0} + \phi_2^0 v_2^{3,0}) = 0 \text{ for } \xi < 0. \tag{3.100}$$

This shows that:

$$\phi_1^0 v_1^{3,0} + \phi_2^0 v_2^{3,0} = C_1 \tag{3.101}$$

where C_1 does not depend on ξ. Since ϕ_i^0 and $v_2^{3,0}$ are independend ot ξ, so is $v_1^{3,0}$. The matching condition yields:

$$v_1^{3,0}(\mathbf{y}_\Gamma, \xi, t) = \lim_{y^3 \to 0-} v_1^{3,0}(\mathbf{y}_\Gamma, y^3, t) \equiv v_{1,-}^{3,0}(\mathbf{y}_\Gamma, t). \tag{3.102}$$

We now examine equations (3.70) and (3.71). The leading order equation only allowed us to show that $v_2^{\alpha,0}$ and $v_\mathrm{f}^{\alpha,0}$ were constant in ξ. To obtain (3.48), we must look at the next order in β. Let us first consider (3.71), or equivalently (3.90). After some calculation, using (3.63), (3.58), (3.60) and (3.93) we obtain:

$$2\zeta \frac{\partial}{\partial \xi}\left(\frac{\partial v_\mathrm{f}^{3,1}}{\partial \xi}\right) - \frac{\partial p^0}{\partial \xi} = \sum_{k=1}^{N} z_k c_k^0 \frac{\partial \psi}{\partial \xi} \text{ for } \xi > 0. \tag{3.103}$$

A similar calculation using (3.70) yields:

$$2\zeta \frac{\partial}{\partial \xi}\left(\eta_2(\phi_{2,-}^0)\frac{\partial v_2^{3,1}}{\partial \xi}\right) - \phi_{2,-}^0 \frac{\partial p^0}{\partial \xi} = \sum_{k=1}^{N} \phi_{2,-}^0 z_k c_k^0 \frac{\partial \psi^0}{\partial \xi} \text{ for } \xi < 0, \tag{3.104}$$

where (3.98) was used to rewrite ϕ_2^0. Using (3.88), the above two equations can be rewritten as follows:

$$\frac{\partial}{\partial \xi}\left(2\zeta \frac{\eta_2(\phi_{2,-}^0)}{\phi_{2,-}^0}\frac{\partial v_2^{3,1}}{\partial \xi} - p^0 + \sum_{k=1}^{N} c_k^0\right) = 0 \text{ for } \xi < 0, \tag{3.105}$$

$$\frac{\partial}{\partial \xi}\left(2\zeta \frac{\partial v_\mathrm{f}^{3,1}}{\partial \xi} - p^0 + \sum_{k=1}^{N} c_k^0\right) = 0 \text{ for } \xi > 0, \tag{3.106}$$

where we also used the fact that $\phi_{2,-}^0$ is independent of ξ (see (3.98)) in the first equality. At $\xi = 0$, we have the following condition from (3.72):

$$\eta_\perp(v^{3,0}_{\mathrm{f},+} - v^{3,0}_{1,-}) = p^0\big|_{\xi=0-} - p^0\big|_{\xi=0+} - 2\zeta\frac{\eta_2(\phi^0_{2,-})}{\phi^0_{2,-}}\frac{\partial v^{3,1}_2}{\partial \xi} + 2\zeta\frac{\partial v^{3,1}_\mathrm{f}}{\partial \xi} \tag{3.107}$$

where we used the definition of w, (3.94) and (3.102) to obtain the left hand side of the above relation. We shall also need the matching condition:

$$\lim_{\xi\to\pm\infty} p^0(\mathbf{y}_\Gamma, \xi, t) = \lim_{y^3\to 0\pm} p^0(\mathbf{y}_\Gamma, y^3, t) \equiv p^0_\pm. \tag{3.108}$$

Let us first consider the (3.106). We immediately have:

$$2\zeta\frac{\partial v^{3,1}_\mathrm{f}}{\partial \xi} - p^0 + \sum_{k=1}^{N} c^0_k = C_2 \tag{3.109}$$

where C_2 does not depend on ξ. Using (3.87) and (3.108), we have:

$$\lim_{\xi\to\infty} 2\zeta\frac{\partial v^{3,1}_\mathrm{f}}{\partial \xi} = C_2 + p^0_+ - \sum_{k=1}^{N} c^0_{k,+}. \tag{3.110}$$

By the l'Hôpital rule, we have:

$$\lim_{\xi\to\infty}\frac{v^{3,1}_\mathrm{f}(\xi)}{\xi} = \frac{1}{2\zeta}\left(C_2 + p^0_+ - \sum_{k=1}^{N} c^0_{k,+}\right) \equiv s_+. \tag{3.111}$$

Therefore, we have:

$$v^{3,1}_\mathrm{f}(\mathbf{y}_\Gamma, \xi, t) = s_+(\mathbf{y}_\Gamma, t)\xi + r,\ \lim_{\xi\to\infty}\frac{r}{\xi} = 0. \tag{3.112}$$

Writing out the inner solution for v^3_f to order β, we have:

$$v^3_\mathrm{f}(\mathbf{y}_\Gamma, \xi, t) = v^{3,0}_{\mathrm{f},+}(\mathbf{y}_\Gamma, t) + \beta s_+(\mathbf{y}_\Gamma, t)\xi + \beta r(\mathbf{y}_\Gamma, \xi, t) + \cdots. \tag{3.113}$$

For the outer solution, we shall simply use the following expression:

$$v^3_\mathrm{f}(\mathbf{y}_\Gamma, y^3, t) = v^{3,0}_\mathrm{f}(\mathbf{y}_\Gamma, y^3, t) + \beta v^{3,1}_\mathrm{f}(\mathbf{y}_\Gamma, y^3, t) + \cdots. \tag{3.114}$$

We now invoke the Kaplun matching procedure [17, 21]. Introduce an intermediate coordinate system η such that:

$$\beta\xi = y^3 = \beta^\alpha \eta, \; 0 < \alpha < 1. \tag{3.115}$$

The matching procedure is to write (3.113) and (3.114) in terms ot η and require that like terms in β be identical. From (3.113), we have:

$$v_\mathrm{f}^3(\mathbf{y}_\Gamma, \beta^{\alpha-1}\eta, t) = v_{\mathrm{f},+}^{3,0}(\mathbf{y}_\Gamma, t) + \beta^\alpha \eta s_+(\mathbf{y}_\Gamma, t) + \beta r(\mathbf{y}_\Gamma, \beta^{\alpha-1}\eta, t) + \cdots . \tag{3.116}$$

From (3.114), we have:

$$v_\mathrm{f}^3(\mathbf{y}_\Gamma, \beta^\alpha \eta, t) = \lim_{y^3 \to 0+} v_\mathrm{f}^{3,0}(\mathbf{y}_\Gamma, y^3, t) + \beta^\alpha \eta \lim_{y^3 \to 0+} \frac{\partial v_\mathrm{f}^{3,0}}{\partial y^3}(\mathbf{y}_\Gamma, y^3, t) + \cdots . \tag{3.117}$$

Comparing the β^0 term simply reproduces (3.93). Comparing the β^α term yields:

$$\lim_{y^3 \to 0+} \frac{\partial v_\mathrm{f}^{3,0}}{\partial y^3}(\mathbf{y}_\Gamma, y^3, t) = s_+(\mathbf{y}_\Gamma, t). \tag{3.118}$$

We may perform a similar calculation on (3.106) to obtain:

$$\begin{aligned} \lim_{y^3 \to 0-} \frac{\partial v_2^{3,0}}{\partial y^3}(\mathbf{y}_\Gamma, y^3, t) &= \frac{\phi_{2,-}}{2\zeta \eta_2(\phi_{2,-})} \left(C_3 + p_-^0 - \sum_{k=1}^N c_{k,-}^0 \right), \\ C_3 &= 2\zeta \frac{\eta_2(\phi_{2,-}^0)}{\phi_{2,-}^0} \frac{\partial v_2^{3,1}}{\partial \xi} - p^0 + \sum_{k=1}^N c_k^0. \end{aligned} \tag{3.119}$$

where C_3 does not depend on ξ. Combining (3.107), (3.109), (3.111), (3.118) and (3.119), we have:

$$\begin{aligned} \eta_\perp (v_{\mathrm{f},+}^{3,0} - v_{1,-}^{3,0}) = p_-^0 - p_+^0 - \sum_{k=1}^N c_{k,-}^0 + \sum_{k=1}^N c_{k,+}^0 \\ - \lim_{y^3 \to 0-} 2\zeta \frac{\eta_2(\phi_2^0)}{\phi_2^0} \frac{\partial v_2^{3,0}}{\partial y^3} + \lim_{y^3 \to 0+} 2\zeta \frac{\partial v_\mathrm{f}^{3,0}}{\partial y^3}. \end{aligned} \tag{3.120}$$

This is nothing other than (3.48).

3.3 Onsager's variational principle for ionic case

We want to apply Onsager's variational principle to derive the dynamic equations. With diffusing ionic species in the model, here, we consider the situation when dielectric constant equals zero. For positive dielectric constant, Onsager's variational principle can be applied in a similar manner and we put the detailed calculation in the appendix I. Let $\mathbf{u}_k$ be the velocity of k-th ion, the *kinematic relations* have to include (2.2), (2.30)-(2.33), together with

$$\frac{\partial(\phi_2 c_k)}{\partial t} + \nabla \cdot (\phi_2 c_k \mathbf{u}_k) = 0 \quad \text{in } \Omega_t; \tag{3.121}$$

$$\frac{\partial c_k}{\partial t} + \nabla \cdot (c_k \mathbf{u}_k) = 0 \quad \text{in } \mathcal{R}_t. \tag{3.122}$$

Notice that (3.3), (3.4) cannot be used here, since the ion velocities have not been derived yet. The *kinematic constraints* have to include (2.3) and (2.9) together with (3.46).

The boundary conditions include the continuities of ion flux across the interface and no flux across the outer surface. Again, we may not simply use $(3.10)_2$ and (3.12); rather, we propose

$$j_k := \phi_2 c_k^+ (\mathbf{u}_k^+ - \mathbf{v}_1) \cdot \mathbf{n} = c_k^- (\mathbf{u}_k^- - \mathbf{v}_1) \cdot \mathbf{n}, \tag{3.123}$$

and on the outer surface $\partial \mathbb{U}$,

$$\mathbf{u}_k \cdot \mathbf{n} = 0. \tag{3.124}$$

Let the potential energy

$$\mathcal{U} = U + E_{\text{ion}} = U + \int_{\Omega_t} \phi_2 \mathcal{W}_{\text{ion}}(c_k) d\mathbf{x} + \int_{\mathcal{R}_t} \mathcal{W}_{\text{ion}}(c_k) d\mathbf{x}, \tag{3.125}$$

satisfy (2.59) and (3.1), let Rayleigh's dissipation function be

$$\begin{aligned} \mathcal{W} =& W + \sum_{k=1}^{N} \int_{\Omega_t} \frac{1}{2} k_B T D_k^{-1} \phi_2^2 c_k |\mathbf{u}_k - \mathbf{v}_2|^2 d\mathbf{x} \\ &+ \sum_{k=1}^{N} \int_{\mathcal{R}_t} \frac{1}{2} k_B T D_k^{-1} c_k |\mathbf{u}_k - \mathbf{v}_{\text{f}}|^2 d\mathbf{x}, \end{aligned} \tag{3.126}$$

in which W is defined in (2.61). Here, the ions flow in the solvent and we assume friction exists between ion and fluid. We ignore the friction between ions, and the friction between ion and polymer network. For body forces, we define $f_{i,\mathrm{f}}$ by (3.6). Notice that outer fluid is electroneutral, hence

$$\mathbf{f}_{\mathrm{f}} = 0.$$

The ionic version of Onsager's variational principle is stated as follows.

Theorem 3.3. *Let $\phi_{1,2}$, $\mathbf{v}_{i,f}$, c_k, $\mathbf{u}_k$, ψ be smooth functions that satisfy* (3.46)*, $\mathcal{U}$ be defined by* (3.125) *and $\dot{\mathcal{U}}$ be defined through the kinematic relations* (2.2)*,* (2.30)*-*(2.33)*,* (3.121)*-*(3.122)*,* (3.46)*(taking time derivative). Let*

$$Z \subset (C^2(\Omega_t))^{N+2} \times (C^2(\mathcal{R}_t))^{N+1} \tag{3.127}$$

be a subspace consisting of all elements $\{\mathbf{u}_1, \cdots, \mathbf{u}_N, \mathbf{v}_{1,2,f}\}$ that (2.3)*,* (2.9)*,* (2.11)*-*(2.13)*,* (2.18)*,* (3.123)*-*(3.124) *are satisfied. Suppose, for some $\{\mathbf{u}_1, \cdots, \mathbf{u}_N, \mathbf{v}_{1,2,f}\}$,* (2.4)*,* (2.8) *with $\gamma_{1,2} = 0$,* (2.34)*,* (2.41)*,* (2.42)*,* (3.6)*,* (2.39) *and boundary conditions* (2.16)*,* $(3.10)_2$ (3.47)*,* (3.48) *are all well defined and satisfied, then this $\{\mathbf{u}_1, \cdots, \mathbf{u}_N, \mathbf{v}_{1,2,f}\}$ minimizes*

$$R = \dot{\mathcal{U}} + \mathcal{W} \tag{3.128}$$

in Z.

Proof. We want to find the necessary conditions that an element of Z minimizes the energy dissipation rate R, subject to the incompressibility condition (2.3), (2.9), and electroneutrality condition (3.46). Accordingly, we try to minimize

$$\begin{aligned}\mathcal{R} = & R - \int_{\Omega_t} p\nabla \cdot (\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) - \psi \frac{\partial}{\partial t}\left(\phi_1 \rho_p + \phi_2 \sum_{k=1}^{N} q z_k c_k\right) d\mathbf{x} \\ & - \int_{\mathcal{R}_t} p\nabla \cdot \mathbf{v}_{\mathrm{f}} - \psi \frac{\partial}{\partial t}\left(\sum_{k=1}^{N} q z_k c_k\right) d\mathbf{x}\end{aligned} \tag{3.129}$$

instead of R. The set of minimizer $\{\mathbf{u}_k,\ \mathbf{v}_{i,\mathrm{f}}\}$ has to satisfy

$$\frac{\delta \mathcal{R}}{\delta \mathbf{u}_k} = \frac{\delta \mathcal{R}}{\delta \mathbf{v}_i} = 0 \quad \text{for} \quad k = 1, \cdots, N;\ i = 1, 2, f.$$

Now we prove the balance equations $(2.4)_{1,2}$ and (2.8) can be derived from the equalities above.

First, we calculate $\dot{\mathcal{U}}$ in Ω_t. For ionic energy, we differentiate the energy form and use (3.121),(3.122) to replace the time derivatives of u_k:

$$
\begin{aligned}
&\frac{d}{dt}\int_{\Omega_t}\phi_2\mathcal{W}_{\text{ion}}d\mathbf{x}\\
=&\int_{\Omega_t}\sum_{k=1}^{N}\phi_2\frac{\partial\mathcal{W}_{\text{ion}}}{\partial c_k}\frac{\partial c_k}{\partial t}+\frac{\partial\phi_2}{\partial t}\mathcal{W}_{\text{ion}}+\nabla\cdot(\phi_2\mathcal{W}_{\text{ion}}\mathbf{v}_1)d\mathbf{x}\\
=&\int_{\Omega_t}\sum_{k=1}^{N}\frac{\partial\mathcal{W}_{\text{ion}}}{\partial c_k}\left(-\nabla\cdot(\phi_2c_k\mathbf{u}_k)-c_k\frac{\partial\phi_2}{\partial t}\right)+\mathcal{W}_{\text{ion}}\left(\frac{\partial\phi_2}{\partial t}+\nabla\cdot(\phi_2\mathbf{v}_1)\right)\\
&+\phi_2\mathbf{v}_1\cdot\nabla\mathcal{W}_{\text{ion}}d\mathbf{x}\\
=&\int_{\Omega_t}\sum_{k=1}^{N}\frac{\partial\mathcal{W}_{\text{ion}}}{\partial c_k}\left(-\nabla\cdot(\phi_2c_k\mathbf{u}_k)+c_k\nabla\cdot(\phi_2\mathbf{v}_2)+\phi_2\nabla c_k\cdot\mathbf{v}_1\right)+\\
&\mathcal{W}_{\text{ion}}\nabla\cdot\left(\phi_2(\mathbf{v}_1-\mathbf{v}_2)\right)d\mathbf{x}\\
=&\sum_{k=1}^{N}\int_{\Omega_t}\nabla\left(\frac{\partial\mathcal{W}_{\text{ion}}}{\partial c_k}\right)\cdot(\phi_2c_k\mathbf{u}_k)-\phi_2\nabla\left(c_k\frac{\partial\mathcal{W}_{\text{ion}}}{\partial c_k}\right)\cdot\mathbf{v}_2+\phi_2\frac{\partial\mathcal{W}_{\text{ion}}}{\partial c_k}\nabla c_k\cdot\mathbf{v}_1\\
&-\phi_2\frac{\partial\mathcal{W}_{\text{ion}}}{\partial c_k}\nabla c_k\cdot(\mathbf{v}_1-\mathbf{v}_2)d\mathbf{x}+\int_{\Gamma_t}\sum_{k=1}^{N}\frac{\partial\mathcal{W}_{\text{ion}}}{\partial c_k}\phi_2c_k(\mathbf{v}_2-\mathbf{u}_k)\cdot\mathbf{n}\\
&+\mathcal{W}_{\text{ion}}\phi_2(\mathbf{v}_1-\mathbf{v}_2)\cdot\mathbf{n}dS\\
=&\sum_{k=1}^{N}\int_{\Omega_t}\phi_2c_k\nabla\left(\frac{\partial\mathcal{W}_{\text{ion}}}{\partial c_k}\right)\cdot\mathbf{u}_k-k_BT\phi_2\nabla c_k\cdot\mathbf{v}_2d\mathbf{x}\\
&+k_BT\sum_{k=1}^{N}\int_{\Gamma_t}\phi_2c_k\ln c_k(\mathbf{v}_1-\mathbf{u}_k)\cdot\mathbf{n}+\phi_2c_k(\mathbf{v}_2-\mathbf{u}_k)\cdot\mathbf{n}dS
\end{aligned}
\tag{3.130}
$$

Similarly for $\mathcal{R}_t$, we get

$$
\begin{aligned}
&\frac{d}{dt}\int_{\mathcal{R}_t}\mathcal{W}_{\text{ion}}d\mathbf{x}\\
=&\sum_{k=1}^{N}\int_{\mathcal{R}_t}c_k\nabla\left(\frac{\partial\mathcal{W}_{\text{ion}}}{\partial c_k}\right)\cdot\mathbf{u}_kd\mathbf{x}+k_BT\sum_{k=1}^{N}\int_{\Gamma_t}c_k\ln c_k(\mathbf{u}_k-\mathbf{v}_1)\cdot\mathbf{n}+c_k(\mathbf{u}_k\cdot\mathbf{n})dS\\
=&\sum_{k=1}^{N}\int_{\mathcal{R}_t}c_k\nabla\left(\frac{\partial\mathcal{W}_{\text{ion}}}{\partial c_k}\right)\cdot\mathbf{u}_kd\mathbf{x}
\end{aligned}
$$

$$
\begin{aligned}
&+ k_BT \sum_{k=1}^{N} \int_{\Gamma_t} c_k \ln c_k(\mathbf{u}_k - \mathbf{v}_1)\cdot\mathbf{n} + c_k(\mathbf{u}_k - \mathbf{v}_\mathrm{f})\cdot\mathbf{n} + c_k(\mathbf{v}_\mathrm{f}\cdot\mathbf{n}) dS \\
=& \sum_{k=1}^{N} \int_{\mathcal{R}_t} c_k \nabla\left(\frac{\partial \mathcal{W}_\mathrm{ion}}{\partial c_k}\right)\cdot\mathbf{u}_k - k_BT\nabla c_k\cdot\mathbf{v}_\mathrm{f} d\mathbf{x} \\
&+ k_BT \sum_{k=1}^{N} \int_{\Gamma_t} c_k \ln c_k(\mathbf{u}_k - \mathbf{v}_1)\cdot\mathbf{n} + c_k(\mathbf{u}_k - \mathbf{v}_\mathrm{f})\cdot\mathbf{n} dS, \qquad (3.131)
\end{aligned}
$$

where the integral on the outside boundary vanishes, due to (3.124). Adding (3.130) and (3.131), we have

$$
\begin{aligned}
&\frac{d}{dt}\int_{\Omega_t} \phi_2 \mathcal{W}_\mathrm{ion} d\mathbf{x} + \frac{d}{dt}\int_{\mathcal{R}_t} \mathcal{W}_\mathrm{ion} d\mathbf{x} \\
=& \sum_{k=1}^{N} \int_{\Omega_t} \phi_2 c_k \nabla\left(\frac{\partial \mathcal{W}_\mathrm{ion}}{\partial c_k}\right)\cdot\mathbf{u}_k - k_BT\phi_2\nabla c_k\cdot\mathbf{v}_2 d\mathbf{x} \\
&+ \sum_{k=1}^{N} \int_{\mathcal{R}_t} c_k \nabla\left(\frac{\partial \mathcal{W}_\mathrm{ion}}{\partial c_k}\right)\cdot\mathbf{u}_k - k_BT\nabla c_k\cdot\mathbf{v}_\mathrm{f} d\mathbf{x} \\
&+ k_BT \sum_{k=1}^{N} \int_{\Gamma_t} \phi_2 c_k^+ \ln c_k^+(\mathbf{v}_1 - \mathbf{u}_k^+)\cdot\mathbf{n} + \phi_2 c_k^+(\mathbf{v}_2 - \mathbf{u}_k^+)\cdot\mathbf{n} \\
&+ c_k^- \ln c_k^-(\mathbf{u}_k^- - \mathbf{v}_1)\cdot\mathbf{n} + c_k^-(\mathbf{u}_k^- - \mathbf{v}_\mathrm{f})\cdot\mathbf{n} dS. \qquad (3.132)
\end{aligned}
$$

On the other hand, the constraints in (3.129) can be simplified by

$$
\begin{aligned}
&\int_{\Omega_t} \psi \frac{\partial}{\partial t}\left(\phi_1\rho_p + \phi_2\sum_{k=1}^{N} q z_k c_k\right) d\mathbf{x} + \int_{\mathcal{R}_t} \psi \frac{\partial}{\partial t}\left(\sum_{k=1}^{N} q z_k c_k\right) d\mathbf{x} \\
=& \int_{\Omega_t} \psi \left(\frac{\partial \phi_1}{\partial t}\rho_p + \sum_{k=1}^{N} q z_k \frac{\partial(\phi_2 c_k)}{\partial t}\right) d\mathbf{x} + \int_{\mathcal{R}_t} \psi \left(\sum_{k=1}^{N} q z_k \frac{\partial c_k}{\partial t}\right) d\mathbf{x} \\
=& -\int_{\Omega_t} \psi\rho_p\nabla\cdot(\phi_1\mathbf{v}_1) + \psi\sum_{k=1}^{N} q z_k \nabla\cdot(\phi_2 c_k\mathbf{u}_k) d\mathbf{x} - \int_{\mathcal{R}_t} \psi\left(\sum_{k=1}^{N} q z_k\nabla\cdot(c_k\mathbf{u}_k)\right) d\mathbf{x} \\
=& \int_{\Omega_t} \phi_1\rho_p\nabla\psi\cdot\mathbf{v}_1 + \phi_2\sum_{k=1}^{N} q z_k c_k\nabla\psi\cdot\mathbf{u}_k d\mathbf{x} + \int_{\mathcal{R}_t} \sum_{k=1}^{N} q z_k c_k\nabla\psi\cdot\mathbf{u}_k d\mathbf{x} \\
&- \int_{\Gamma_t} \phi_1\rho_p\psi^+(\mathbf{v}_1\cdot\mathbf{n}) + \phi_2\sum_{k=1}^{N} q z_k c_k\psi^+(\mathbf{u}_k^+\cdot\mathbf{n}) - \sum_{k=1}^{N} q z_k c_k\psi^-(\mathbf{u}_k^-\cdot\mathbf{n}) dS \qquad (3.133)
\end{aligned}
$$

where (3.121) and (3.122) are used on the second line, (3.124) are used on the last line. Moreover,

$$
\begin{aligned}
&-\int_{\Omega_t} p\nabla\cdot(\phi_1\mathbf{v}_1+\phi_2\mathbf{v}_2)d\mathbf{x}-\int_{\mathcal{R}_t} p\nabla\cdot\mathbf{v}_{\mathrm{f}}d\mathbf{x}\\
=&\int_{\Omega_t}(\phi_1\mathbf{v}_1+\phi_2\mathbf{v}_2)\cdot\nabla p d\mathbf{x}+\int_{\mathcal{R}_t}\mathbf{v}_{\mathrm{f}}\cdot\nabla p d\mathbf{x}\\
&+\int_{\Gamma_t}-p^+(\phi_1\mathbf{v}_1+\phi_2\mathbf{v}_2)\cdot\mathbf{n}+p^-(\mathbf{v}_{\mathrm{f}}\cdot\mathbf{n})dS. \qquad (3.134)
\end{aligned}
$$

Recall (3.125)-(3.129), we now collect (3.132)-(3.134) and (2.64)-(2.65), to derive:

$$
\begin{aligned}
\mathcal{R}=&\int_{\Omega_t}-\nabla\cdot(\mathcal{T}_1+\mathcal{S}_g)\cdot\mathbf{v}_1-(\nabla\cdot\mathcal{T}_2)\cdot\mathbf{v}_2+\sum_{k=1}^N\phi_2c_k\nabla\left(\frac{\partial\mathcal{W}_{\mathrm{ion}}}{\partial c_k}\right)\cdot(\mathbf{u}_k-\mathbf{v}_2)\\
&+\frac{1}{2}\kappa|\mathbf{v}_1-\mathbf{v}_2|^2+\sum_{k=1}^N\frac{1}{2}k_BTD_k^{-1}\phi_2^2c_k|\mathbf{u}_k-\mathbf{v}_2|^2+\phi_1\rho_p\nabla\psi\cdot\mathbf{v}_1\\
&+\phi_2\sum_{k=1}^N qz_kc_k\nabla\psi\cdot\mathbf{u}_k+(\phi_1\mathbf{v}_1+\phi_2\mathbf{v}_2)\cdot\nabla p\, d\mathbf{x}\\
&+\int_{\mathcal{R}_t}-(\nabla\cdot\mathcal{T}_{\mathrm{f}})\cdot\mathbf{v}_{\mathrm{f}}+\sum_{k=1}^N c_k\nabla\left(\frac{\partial\mathcal{W}_{\mathrm{ion}}}{\partial c_k}\right)\cdot\mathbf{u}_k-\sum_{k=1}^N k_BT\nabla c_k\cdot\mathbf{v}_{\mathrm{f}}\\
&+\sum_{k=1}^N\frac{1}{2}k_BTD_k^{-1}c_k|\mathbf{u}_k-\mathbf{v}_{\mathrm{f}}|^2+\sum_{k=1}^N qz_kc_k\nabla\psi\cdot\mathbf{u}_k+\mathbf{v}_{\mathrm{f}}\cdot\nabla p\, d\mathbf{x}\\
&+\int_{\Gamma_t}-\phi_1\rho_p\psi^+(\mathbf{v}_1\cdot\mathbf{n})-\phi_2\sum_{k=1}^N qz_kc_k\psi^+(\mathbf{u}_k^+\cdot\mathbf{n})+\sum_{k=1}^N qz_kc_k\psi^-(\mathbf{u}_k^-\cdot\mathbf{n})\\
&+k_BT\sum_{k=1}^N\Big(\phi_2c_k^+\ln c_k^+(\mathbf{v}_1-\mathbf{u}_k^+)\cdot\mathbf{n}+\phi_2c_k^+(\mathbf{v}_2-\mathbf{u}_k^+)\cdot\mathbf{n}\\
&+c_k^-\ln c_k^-(\mathbf{u}_k^--\mathbf{v}_1)\cdot\mathbf{n}+c_k^-(\mathbf{u}_k^--\mathbf{v}_{\mathrm{f}})\cdot\mathbf{n}\Big)\, dS+A \text{ in (2.65)}. \qquad (3.135)
\end{aligned}
$$

The partial derivative of $\mathcal{R}$ with respect to $\mathbf{u}_k$ gives the expression of $\mathbf{u}_k$ in Ω_t and $\mathcal{R}_t$:

$$
0=\frac{\delta\mathcal{R}}{\delta\mathbf{u}_k}=\begin{cases}k_BTD_k^{-1}\phi_2^2c_k(\mathbf{u}_k-\mathbf{v}_2)+\phi_2c_k\nabla\left(\frac{\partial\mathcal{W}_{\mathrm{ion}}}{\partial c_k}\right)+\phi_2qz_kc_k\nabla\psi & \text{in } \Omega_t;\\ k_BTD_k^{-1}c_k(\mathbf{u}_k-\mathbf{v}_{\mathrm{f}})+c_k\nabla\left(\frac{\partial\mathcal{W}_{\mathrm{ion}}}{\partial c_k}\right)+qz_kc_k\nabla\psi & \text{in } \mathcal{R}_t.\end{cases}
$$

Consequently,

$$\mathbf{u}_k = \begin{cases} \mathbf{v}_2 - \frac{D_k}{\phi_2 k_B T}\left(\nabla\left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k}\right) + qz_k\nabla\psi\right) & \text{in } \Omega_t; \\ \mathbf{v}_{\text{f}} - \frac{D_k}{k_B T}\left(\nabla\left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k}\right) + qz_k\nabla\psi\right) & \text{in } \mathcal{R}_t. \end{cases} \tag{3.136}$$

Therefore, from (3.121) and (3.122) we derive

$$\frac{\partial}{\partial t}(\phi_2 c_k) + \nabla\cdot(\mathbf{v}_2\phi_2 c_k) = \nabla\cdot\left(\frac{D_k c_k}{k_B T}\nabla\mu_k\right), \tag{3.137}$$

$$\frac{\partial c_k}{\partial t} + \nabla\cdot(\mathbf{v}_{\text{f}} c_k) = \nabla\cdot\left(\frac{D_k c_k}{k_B T}\nabla\mu_k\right). \tag{3.138}$$

Similarly for $\mathbf{v}_1$,

$$0 = \frac{\delta\mathcal{R}}{\delta\mathbf{v}_1} = -\nabla\cdot(\mathcal{T}_1 + \mathcal{S}_g) + \kappa(\mathbf{v}_1 - \mathbf{v}_2) + \phi_1\nabla p - f_1^{\text{elec}},$$

and $(2.4)_1$ follows. For $\mathbf{v}_2$,

$$\begin{aligned} 0 = \frac{\delta\mathcal{R}}{\delta\mathbf{v}_2} =& -\nabla\cdot\mathcal{T}_2 + \kappa(\mathbf{v}_2 - \mathbf{v}_1) + \phi_2\nabla p \\ & - \sum_{k=1}^{N}\phi_2 c_k\nabla\left(\frac{\partial\mathcal{W}_{ion}}{\partial c_k}\right) - \sum_{k=1}^{N} k_B T D_k^{-1}\phi_2^2 c_k(\mathbf{v}_2 - \mathbf{u}_k), \end{aligned}$$

and apply (3.136) to derive $(2.4)_2$. For $\mathbf{v}_{\text{f}}$,

$$0 = \frac{\delta\mathcal{R}}{\delta\mathbf{v}_{\text{f}}} = -\nabla\cdot\mathcal{T}_{\text{f}} + \nabla p + \sum_{k=1}^{N} k_B T D_k^{-1} c_k(\mathbf{v}_{\text{f}} - \mathbf{u}_k) - k_B T\sum_{k=1}^{N}\nabla c_k,$$

and apply (3.136) to derive (2.8).

Lastly, we turn to the boundary terms. From (3.135), the boundary integrals are

$$\begin{aligned} A + \int_{\Gamma_t} & -\phi_1\rho_p\psi^+(\mathbf{v}_1\cdot\mathbf{n}) - \sum_{k=1}^{N} qz_k\phi_2 c_k^+\psi^+(\mathbf{u}_k^+\cdot\mathbf{n}) + \sum_{k=1}^{N} qz_k c_k^-\psi^-(\mathbf{u}_k^-\cdot\mathbf{n}) \\ & + k_B T\sum_{k=1}^{N}\Big(\phi_2 c_k^+\ln c_k^+(\mathbf{v}_1 - \mathbf{u}_k^+)\cdot\mathbf{n} + \phi_2 c_k^+(\mathbf{v}_2 - \mathbf{u}_k^+)\cdot\mathbf{n} \end{aligned}$$

$$
\begin{aligned}
&+ c_k^- \ln c_k^- (\mathbf{u}_k^- - \mathbf{v}_1)\cdot\mathbf{n} + c_k^-(\mathbf{u}_k^- - \mathbf{v}_{\mathrm{f}})\cdot\mathbf{n}\Big) dS \\
=& A + \int_{\Gamma_t} \sum_{k=1}^N q z_k \phi_2 c_k^+ \psi^+ (\mathbf{v}_1 - \mathbf{u}_k^+)\cdot\mathbf{n} + \sum_{k=1}^N q z_k c_k^- \psi^- (\mathbf{u}_k^- - \mathbf{v}_1)\cdot\mathbf{n} \\
&+ k_B T \sum_{k=1}^N \Big(- [\ln c_k]\cdot j_k + \phi_2 c_k^+ (\mathbf{v}_2 - \mathbf{v}_1)\cdot\mathbf{n} + \phi_2 c_k^+ (\mathbf{v}_1 - \mathbf{u}_k^+)\cdot\mathbf{n} \\
&+ c_k^- (\mathbf{u}_k^- - \mathbf{v}_1)\cdot\mathbf{n} + c_k^- (\mathbf{v}_1 - \mathbf{v}_{\mathrm{f}})\cdot\mathbf{n}\Big) dS \\
=& A + \int_{\Gamma_t} \sum_{k=1}^N \Big(- [q z_k \psi]\cdot j_k - [k_B T \ln c_k]\cdot j_k \Big) \\
&+ k_B T \sum_{k=1}^N \Big(\phi_2 c_k^+ (\mathbf{v}_2 - \mathbf{v}_1) + c_k^- (\mathbf{v}_1 - \mathbf{v}_{\mathrm{f}})\cdot\mathbf{n}\Big) dS \\
=& A + \int_{\Gamma_t} \sum_{k=1}^N \Big(- [\mu_k]\cdot j_k + k_B T\, [c_k]\cdot w\Big) dS
\end{aligned}
$$

Now, similar to the proof of theorem 2.2, it is easy to obtain the boundary conditions (2.16), (2.45), (3.47) and (3.48), and the nessessity indicates the minimization. The proof is complete. □

3.4 One-dimensional stability analysis of ionic model

We continue the stability analysis on the one-dimensional model in this section, with ion species coming into play. The gel lies in $x \in (0, a) \subset (0, L)$ and fixed at $x = 0$. We use the same notations as in section 2.4, and the constitutive equations (2.1)-(2.4), (2.8)-(2.9), and boundary conditions (2.11)-(2.13), (2.16), (2.18), (2.44) together with ionic equations (3.3)-(3.4), (3.46), boundary conditions (3.123)-(3.124), (3.47) and (3.48). We start the stability analysis by first introducing the primed dimensionless variables:

$$
\begin{aligned}
&x = 1_L x',\ D_k = D_0 D_k',\ t = \frac{1_L^2}{D_0} t',\ c_k = c_0 c_k',\ \psi = \frac{k_B T}{q}\psi',\ \rho_p = q c_0 \rho_p', \\
&\kappa = 1_\kappa \kappa',\ f = \frac{k_B T}{1_L^3} f'.
\end{aligned} \tag{3.139}
$$

where 1_L is the unit length, 1_κ is the unit friction coefficient, c_0 and D_0 are the representative concentrations and diffusion coefficient, respectively. In the following, the prime symbols are dropped for notational convenience. We state the nondimensionalized equations as follows:

At $x = 0$,

$$v_1 = v_2 = 0; \tag{3.140}$$

$$u_k = v_2 - \frac{D_k}{\phi_2}\left(\frac{(c_k)_x}{c_k} + z_k\psi_x\right) = 0, \tag{3.141}$$

in $(0, a)$,

$$\phi_1 + \phi_2 = 1; \tag{3.142}$$

$$\frac{\partial \phi_1}{\partial t} + (v_1\phi_1)_x = 0; \tag{3.143}$$

$$(\phi_1 v_1 + \phi_2 v_2)_x = 0; \tag{3.144}$$

$$(\eta_1 v_{1,x})_x + (f - \phi_1 f')_x - \phi_1 p_x - \phi_1 \rho_p \psi_x + \kappa(v_2 - v_1) = 0; \tag{3.145}$$

$$(\eta_2 v_{2,x})_x - \phi_2 p_x - \left(\sum_{k=1}^{N} z_k \phi_2 c_k\right)\psi_x + \kappa(v_1 - v_2) = 0; \tag{3.146}$$

$$\frac{\partial}{\partial t}(\phi_2 c_k) + (v_2\phi_2 c_k)_x = \left(D_k (c_k)_x + D_k c_k z_k \psi_x\right)_x; \tag{3.147}$$

$$\phi_1\rho_p + \sum_{k=1}^{N} z_k \phi_2 c_k = 0 \tag{3.148}$$

while at $x = a$:

$$\dot{a} = v_1(x = a); \tag{3.149}$$

$$v_{\mathrm{f}} - v_1 = \phi_2(v_2 - v_1); \tag{3.150}$$

$$\eta_{\mathrm{f}}(v_{\mathrm{f}})_x - \eta_1(v_1)_x - (f - \phi_1 f') - \eta_2(v_2)_x + [p] = 0; \tag{3.151}$$

$$[\mu_k] = [\ln c_k + z_k\psi] = 0; \tag{3.152}$$

$$[j_k] = [c_k]\cdot w - [D_k(c_k)_x + D_k c_k z_k \psi_x] = 0; \tag{3.153}$$

$$\eta_\perp(v_{\mathrm{f}} - v_1) = \eta_{\mathrm{f}}(v_{\mathrm{f}})_x - \phi_2^{-1}\eta_2(v_2)_x + [p] - \sum_{k=1}^{N}[c_k] \quad \text{at } x = a \tag{3.154}$$

and in (a, L),

$$(v_{\mathrm{f}})_x = 0; \tag{3.155}$$

$$(\eta_{\mathrm{f}} v_{\mathrm{f},x})_x - p_x = 0; \tag{3.156}$$

$$\frac{\partial c_k}{\partial t} + (v_{\mathrm{f}} c_k)_x = (D_k (c_k)_x + D_k c_k z_k \psi_x)_x \,; \tag{3.157}$$

$$\sum_{k=1}^{N} z_k c_k = 0 \tag{3.158}$$

while at $x = L$:

$$v_{\mathrm{f}} = 0; \tag{3.159}$$

$$u_k = v_{\mathrm{f}} - \frac{D_k}{c_k}(c_k)_x - D_k z_k \psi_x = 0; \tag{3.160}$$

We turn to the fluid region first. From (3.155), (3.156) and (3.159),

$$v_{\mathrm{f}} = 0 \text{ in } (a, L), \quad p = \text{const.}, \quad \phi_1 v_1 + \phi_2 v_2 = 0 \text{ in } (0, a), \tag{3.161}$$

the last identity comes from (3.150). We assume $p = 0$ in (a, L). Then, from (3.145)-(3.146) and boundary conditions (3.151), we get

$$p = \eta_1 (v_1)_x + \eta_2 (v_2)_x + (f - \phi_1 f') \quad \text{in } (0, a). \tag{3.162}$$

Now (3.140)-(3.160) are simplified to be the following system (†) for $\{\phi_1, v_1, \psi, c_k\}$:

At $x = 0$,

$$v_1 = 0; \tag{3.163}$$

$$(c_k)_x + z_k c_k \psi_x = 0; \tag{3.164}$$

in $(0, a)$,

$$\frac{\partial \phi_1}{\partial t} + (v_1 \phi_1)_x = 0; \tag{3.165}$$

$$(\eta_1 v_{1,x})_x + (f - \phi_1 f')_x + \frac{\phi_1}{1 - \phi_1}\left(\eta_2 \left(\frac{\phi_1 v_1}{1 - \phi_1}\right)_x\right)_x - \frac{\phi_1 \rho_p}{1 - \phi_1}\psi_x = \frac{\kappa v_1}{(1 - \phi_1)^2}; \tag{3.166}$$

$$\frac{\partial}{\partial t}((1 - \phi_1) c_k) - (v_1 \phi_1 c_k)_x = (D_k (c_k)_x + D_k c_k z_k \psi_x)_x \,; \tag{3.167}$$

$$\phi_1\rho_p + \sum_{k=1}^{N} z_k\phi_2 c_k = 0 \tag{3.168}$$

while at $x = a$:

$$[c_k]\cdot v_1 + [D_k(c_k)_x + D_k c_k z_k \psi_x] = 0; \tag{3.169}$$

$$[\ln c_k + z_k\psi] = 0; \tag{3.170}$$

$$-\eta_\perp v_1 = \frac{\phi_1\eta_2}{1-\phi_1}\left(\frac{\phi_1 v_1}{1-\phi_1}\right)_x + \eta_1(v_1)_x + (f - \phi_1 f') - \sum_{k=1}^{N}[c_k] \quad \text{at } x = a \tag{3.171}$$

and in (a, L),

$$\frac{\partial c_k}{\partial t} = (D_k(c_k)_x + D_k c_k z_k \psi_x)_x\,; \tag{3.172}$$

$$\sum_{k=1}^{N} z_k c_k = 0 \tag{3.173}$$

while at $x = L$:

$$(c_k)_x + c_k z_k \psi_x = 0. \tag{3.174}$$

Remark 3.1. *We assume the diffusion coefficient D_k to be constant in the outside fluid; however, in the gel region D_k depends on ϕ_1. Usually, they are equal when $\phi_1 = 0$. In Tanaka and Filmore [], D_k is inversely proportional to the friction coefficient.*

3.4.1 Steady state solution

We look for solution of (†) when $v_1 \equiv 0$. Like the mechanical case, we only consider generic cases that the gel does not expand and occupy the whole domain.

Theorem 3.4. *Suppose the length L in the system (†) is large enough that the gel does not expand to the whole domain. Then (†) has a unique steady state solution:*

$$\phi_1 = \phi_0, \quad \psi = \begin{cases} \psi_0^+ & \text{in } (0,a); \\ \psi_0^- & \text{in } (a,L), \end{cases} \quad \text{and } c_k = \zeta_k \cdot e^{-z_k\psi}, \tag{3.175}$$

in which $1 > \phi_0 > 0$, ψ_0^+, ψ_0^-, $\zeta_k > 0$ are constants, ζ_k determined by the initial *concentration. Let* $\psi_0^- = 0$, $l = a$, *the solution* (3.175) *is unique.*

Proof. Let $A_k = \int_0^L c_k(x)dx$ be the total concentration of k-th ion, and $l_0 = \int_0^a \phi_1(x)dx < l$ be the essential length of polymer. We need to prove, for any initial data $\{A_1, \cdots, A_N, l_0\}$ such that neutrality constraint

$$\sum_{k=1}^{N} z_k A_k + \rho_p l_0 = 0 \tag{3.176}$$

is satisfied, the statement must be true.

Let $\phi_1 = \phi_1(x)$, $\psi = \psi(x)$, $c_k = c_k(x)$, and let $v_1 \equiv 0$. Let $\psi = 0$ at $x = L$. From (3.167), (3.169), (3.172) and (3.174),

$$D_k(c_k)_x + D_k c_k z_k \psi_x = 0 \quad \text{hence} \quad (c_k)_x + c_k z_k \psi_x = 0 \quad \text{in} \quad (0, L). \tag{3.177}$$

Therefore,

$$c_k = \zeta_k e_k, \quad e_k := e_k(\psi) = e^{-z_k \psi}, \tag{3.178}$$

ζ_k being constant in $(0, L)$. It follows from (3.173) that $\psi \equiv 0$ in (a, L). To show ψ is constant in $(0, a)$, we let

$$\begin{aligned} g(\psi) &= -\sum_{k=1}^{N} z_k c_k = -\sum_{k=1}^{N} z_k \zeta_k e_k, \\ g'(\psi) &= \sum_{k=1}^{N} z_k^2 \zeta_k e_k > 0. \end{aligned} \tag{3.179}$$

Now from (3.168), $\phi_1 = \frac{g}{\rho_p + g}$, and (3.166) becomes

$$\phi_1 \rho_p \left(f''(\phi_1) \cdot \frac{g'(\psi)}{(\rho_p + g(\psi))^2} + \frac{1}{1 - \phi_1} \right) \psi_x = 0. \tag{3.180}$$

Since $g'(\psi) > 0$, we have $\psi_x = 0$ in $(0, a)$ hence ψ and ϕ_1 are both constants in $(0, a)$. Therefore, from definition of A_k, we derive

$$((L - l) \cdot 1 + l \cdot (1 - \phi_1) e_k) \zeta_k = A_k, \quad \text{or} \quad \zeta_k = \frac{A_k}{L - l + l(1 - \phi_1) e_k}, \tag{3.181}$$

and (†) is reduced to

$$f(\phi_1) - \phi_1 f'(\phi_1) = \sum_{k=1}^{N} \frac{A_k(e_k - 1)}{L - l + l(1 - \phi_1)e_k}; \tag{3.182}$$

$$\sum_{k=1}^{N} \frac{z_k A_k}{L - l + l(1 - \phi_1)e_k} = 0; \tag{3.183}$$

$$l\phi_1 = l_0, \quad \phi_1 = \frac{g(\psi)}{\rho_p + g(\psi)}; \tag{3.184}$$

$$\sum_{k=1}^{N} z_k A_k + \rho_p l_0 = 0. \tag{3.185}$$

Notice $\rho_p < 0$, and $g(0) = -\sum_{k=1}^{N} \frac{z_k A_k}{L} = \frac{\rho_p l_0}{L} < 0$ from (3.185). Therefore, in (3.184), if $\psi = 0$,

$$l\phi_1 = l \cdot \frac{g(0)}{\rho_p + g(0)} = \frac{l \cdot l_0}{L + l_0} < l_0, \tag{3.186}$$

and since $g(\psi)$ is strictly increasing, it follows $\psi < 0$ in $(0, a)$. Then

$$l = \frac{l_0}{\phi_1} = \frac{l_0(\rho_p + g(\psi))}{g(\psi)}, \quad \frac{dl}{d\psi} = -\frac{l_0 \rho_p g'(\psi)}{g^2(\psi)} > 0, \text{ and } \frac{d\phi_1}{d\psi} < 0,$$

meaning in (3.183), as l increases, the solution for ψ increases, too. Finally, we turn to (3.182). It is easy to see left hand side is strictly increasing in ψ, if it can be shown right hand side is strictly decreasing, then there is a unique solution and the proof is complete, so we focus on the right hand side:

$$\begin{aligned}
&\frac{d}{d\psi}\sum_{k=1}^{N}\frac{A_k(e_k-1)}{L-l+l(1-\phi_1)e_k}\\
=&-\sum_{k=1}^{N}A_k\cdot\frac{z_ke_kL+(e_k-1)^2\frac{dl}{d\psi}}{(L-l+l(1-\phi_1)e_k)^2}\\
<&-\sum_{k=1}^{N}A_k\cdot\frac{z_ke_kL}{(L-l+l(1-\phi_1)e_k)^2}\quad(\text{since }\ \frac{dl}{d\psi}>0)\\
=&-\sum_{k=1}^{N}\frac{A_kL}{L-l+l(1-\phi_1)e_k}\cdot\frac{z_ke_k}{L-l+l(1-\phi_1)e_k}\\
<&-\sum_{k=1}^{N}\frac{A_kL}{L-l+l(1-\phi_1)e_k}\cdot\frac{z_k}{L-l_0}\quad(\text{since }\ \frac{z_ke_k}{L-l+l(1-\phi_1)e_k}>\frac{z_k}{L-l_0}\ \ \forall k)\\
=&-\frac{L}{L-l_0}\sum_{k=1}^{N}\frac{z_kA_k}{L-l+l(1-\phi_1)e_k}=0
\end{aligned}\tag{3.187}$$

the last equality comes from (3.183). If (3.182) does not have a solution, ϕ_1 keeps decreasing and the gel will occupy the whole domain. Therefore we assume (3.182) does have a solution as $\psi=\psi_0^+$ and $\phi_1=\phi_0$, the conclusion follows. □

We rewrite (3.182)-(3.184) for convenient referrals:

$$f(\phi_0)-\phi_1f'(\phi_0)=\sum_{k=1}^{N}\zeta_k(e_k-1);\tag{3.188}$$

$$\sum_{k=1}^{N}z_k\zeta_k=0;\tag{3.189}$$

$$\phi_0=\frac{g(\psi_0)}{\rho_p+g(\psi_0)},\quad g(\psi_0)=-\sum_{k=1}^{N}z_k\zeta_ke_k,\quad\text{or}\quad\rho_p=-\frac{1-\phi_0}{\phi_0}\sum_{k=1}^{N}z_k\zeta_ke_k\tag{3.190}$$

in which $e_k:=e^{-z_k\psi_0}$ and use e_k globally when no confusion occurs. Then $c_k=\zeta_ke_k$ from (3.175).

Consider a small perturbation of the system (†) near the equilibrium defined by

(3.175), (3.188)-(3.190)

$$x = \varphi_t(X) = X + \epsilon u(X,t) + O(\epsilon^2), \quad \epsilon \ll 1, \tag{3.191}$$

$$\begin{aligned} c_k &= \zeta_k e^{-z_k\psi_0 + \epsilon^\alpha z_k d_k} + O(\epsilon^\alpha) \\ &= \zeta_k e_k\left(1 + \epsilon^\alpha z_k d_k\right) + O(\epsilon^\alpha), \quad \alpha > 0; \end{aligned} \tag{3.192}$$

$$\psi = \psi_0 + \epsilon^\beta \psi_1 + O(\epsilon^\beta), \quad \beta > 0, \tag{3.193}$$

in which we use $e^{\epsilon\tau} = 1 + \epsilon\tau + O(\epsilon)$. Similar to (2.85), we have (2.86). Moreover, from (3.167), (3.172) and (3.174), we have $\alpha = \beta$; from (3.169), we have $\alpha = 1$. Apply (3.191), (3.192) and (3.193) with $\alpha, \beta = 1$ to the system (†), and use (3.175), (3.188)-(3.190), we derive the following system (‡) of equations and boundary conditions for $\{u, d_k, \psi_1\}$.

At $x = 0$,

$$u = 0, \quad (d_k^+ + \psi_1^+)_x = 0; \tag{3.194}$$

in $(0, a)$,

$$Hu_{txx} + \phi_0^2 f''(\phi_0) u_{xx} = \frac{\kappa}{(1-\phi_0)^2} u_t + \frac{\phi_0 \rho_p}{1-\phi_0} (\psi_1^+)_x; \tag{3.195}$$

$$\frac{\partial d_k^+}{\partial t} = \frac{D_k^+}{1-\phi_0}\left(d_k^+ + \psi_1^+\right)_{xx}; \tag{3.196}$$

$$\sum_{k=1}^N z_k^2 \zeta_k e_k^+ d_k^+ = \frac{\phi_0 \rho_p}{(1-\phi_0)^2} u_x \tag{3.197}$$

while at $x = a$:

$$u_t(e_k^+ - e_k^-) + z_k\left[D_k e_k (d_k + \psi_1)_x\right] = 0; \tag{3.198}$$

$$[d_k + \psi_1] = 0; \tag{3.199}$$

$$-\eta_\perp u_t = Hu_{tx} + \phi_0^2 f''(\phi_0) u_x - \sum_{k=1}^N z_k \zeta_k \left[e_k d_k\right] \quad \text{at } \; x = a \tag{3.200}$$

and in (a, L),

$$\frac{\partial d_k^-}{\partial t} = D_k^-\left(d_k^- + \psi_1^-\right)_{xx}; \tag{3.201}$$

$$\sum_{k=1}^N z_k^2 \zeta_k e_k^- d_k^- = 0 \tag{3.202}$$

while at $x = L$:

$$(d_k^- + \psi_1^-)_x = 0, \tag{3.203}$$

in which $H = \eta_1 + \phi_0^2(1-\phi_0)^{-2}\eta_2$ stands for the viscosity coefficient of the mixture, and ϕ_0, ψ_0 satisfy (3.188)-(3.190).

Remark 3.2. *For convenience of computations hereafter, we use notations defined in* (3.191)-(3.193). *If one lets* $c_k = c_{k,0} + \epsilon c_{k,1} + O(\epsilon^2)$, *then* (3.196) *and* (3.197) *become*

$$\frac{\partial c_{k,1}}{\partial t} = \frac{D_k^+}{1-\phi_0}(c_{k,1}^+ + c_{k,0} z_k \psi_1^+)_{xx};$$
$$\sum_{k=1}^{N} z_k c_{k,1}^+ = \frac{\phi_0 \rho_p}{(1-\phi_0)^2} u_x$$

and similar for the other equations.

The system (‡) also satisfies a linearized version of energy dissipation identity:

$$\begin{aligned}
&\frac{d}{dt}\left(\frac{1}{2}\phi_0^2 f''(\phi_0)\int_0^a u_x^2 dx\right) + \frac{d}{dt}\left(\sum_{k=1}^{N}\frac{1}{2}(1-\phi_0) z_k^2 \zeta_k e_k^+ \int_0^a (d_k^+)^2 dx\right)\\
&+\frac{d}{dt}\left(\sum_{k=1}^{N}\frac{1}{2} z_k^2 \zeta_k e_k^- \int_a^L (d_k^-)^2 dx\right) = -H\int_0^a (u_{tx})^2 dx\\
&-\frac{\kappa}{(1-\phi_0)^2}\int_0^a u_t^2 dx - \sum_{k=1}^{N} z_k^2 \zeta_k \int_0^L D_k e_k (d_k + \psi_1)_x^2 dx - \eta_\perp u_t(a)^2.
\end{aligned} \tag{3.204}$$

We briefly sketch the proof here. Multiply (3.195) by u_t and integrate by parts, and apply (3.194), (3.200) on the boundary terms. Multiply (3.196) by $(1-\phi_0)z_k^2\zeta_k e_k^+(d_k^+ + \psi_1^+)$ and multiply (3.201) by $z_k^2\zeta_k e_k^-(d_k^- + \psi_1^-)$ and integrate. Differentiate (3.197) w.r.t. t and multiply by $(1-\phi_0)\psi_1^+$ and integrate, and similarly for (3.202). Use (3.190) to replace ρ_p and add all the equations above. The boundary terms at $x = a$ will all vanish due to (3.198)-(3.199), except $\eta_\perp u_t^2$. The remaining terms exactly form (3.204).

3.4.2 Minimum decay rate: a simple case

A simple case is when the diffusion coefficients D_k's are extremely large in the outside fluid, which forces $d_k \equiv 0$, $\psi_1 \equiv 0$ in (a, L). Let

$$u(x,t) = e^{-\lambda t}\widetilde{u}(x), \quad \psi_1(x,t) = e^{-\lambda t}\widetilde{\psi_1}(x), \quad d_k = e^{-\lambda t}\widetilde{d}_k(x), \text{ and } v(x) = -\widetilde{u}_x(x). \tag{3.205}$$

Then from (‡) we derive the following reduced system: in $(0, a)$,

$$(-\lambda H + \phi_0^2 f''(\phi_0))v_{xx} = -\frac{\lambda\kappa}{(1-\phi_0)^2}v + \frac{\phi_0\rho_p}{1-\phi_0}(\psi_1)_{xx}; \tag{3.206}$$

$$-\lambda d_k = \frac{D_k}{1-\phi_0}(d_k + \psi_1)_{xx}; \tag{3.207}$$

$$\sum_{k=1}^{N} z_k^2\zeta_k e_k d_k = -\frac{\phi_0\rho_p}{(1-\phi_0)^2}v; \tag{3.208}$$

while

$$(d_k + \psi_1)_x = 0, \qquad x = 0; \tag{3.209}$$

$$d_k = 0, \quad \psi_1 = 0, \quad x = a \tag{3.210}$$

in which we have dropped the tildes for notational convenience. We consider a single mode perturbation, letting $\psi_1 = \cos\omega(x-\alpha)$. Before proceeding further, We have to eliminate the case when resonance occurs.

Lemma 3.1. *Let* $\{\lambda, v, d_k, \psi_1\}$ *satisfy equations* (3.206)-(3.210)*, then*

$$\lambda \neq \frac{\phi_0^2 f''(\phi_0)}{\frac{\kappa}{(1-\phi_0)^2\omega^2} + H}, \ \frac{D_k\omega^2}{1-\phi_0}, \ k = 1, \cdots, N. \tag{3.211}$$

Proof. If $\lambda = \frac{D_k\omega^2}{1-\phi_0}$, from (3.207), d_k contains $x\sin\omega(x-\alpha)$ term, but then (3.210) cannot hold. This means $\lambda \neq \frac{D_k\omega^2}{1-\phi_0}$ for any $k = 1, \cdots, N$ and no resonance term appears in d_k. Now if $\lambda = \frac{\phi_0^2 f''(\phi_0)}{\frac{\kappa}{(1-\phi_0)^2\omega^2}+H}$, from (3.206), v contains $x\cos\omega(x-\alpha)$ term, but then (3.208) cannot hold. □

The following theorem gives the equation of eigenvalues, and an estimate on the principal one.

Theorem 3.5. *Let* $\{\lambda, v, d_k, \psi_1\}$ *satisfy equations* (3.206)-(3.210). *The solutions of the following equations,*

$$\frac{\phi_0^2\rho_p^2}{(1-\phi_0)((\kappa+(1-\phi_0)^2H\omega^2)\lambda-\phi_0^2(1-\phi_0)^2f''(\phi_0)\omega^2)}+\sum_{k=1}^{N}\frac{D_kz_k^2\zeta_ke_k}{(1-\phi_0)\lambda-D_k\omega^2}=0. \tag{3.212}$$

in which ω *takes values as* $(n+\frac{1}{2})\frac{\pi}{a}$, $n\in\mathbb{N}\cup\{0\}$, *consist of all eigenvalues* λ *defined in* (3.206)-(3.210). *Particularly, let* λ_1 *be the smallest solution of* (3.212) *among all* ω*'s, it satisfies the equation with* $\omega=\frac{\pi}{2a}$. *Furthermore, if we let*

$$\gamma_1=\min\{\frac{\phi_0^2f''(\phi_0)}{\frac{4\kappa a^2}{(1-\phi_0)^2\pi^2}+H},\ \frac{D_k\pi^2}{4(1-\phi_0)a^2},\ k=1,\cdots,N\}, \tag{3.213}$$

and let γ_2 *be the second smallest. Then* $\lambda_1\in(\gamma_1,\gamma_2)$.

When $N>4$, (3.212) is essentially a polynomial of degree N which has no explicit formula. $\lambda_1\in(\gamma_1,\gamma_2)$ gives a proper estimate.

It is not necessary to assume PEP and PEIs are distinct. If any two or more of them are equal, simply there are fewer roots of (3.212). However, we cannot treat them as one ion species when the valences are different. The extreme case occurs when PEP and all PEIs are equal. In this case, D_k's are all equal and (3.208) cannot hold. This means the mode with frequency $\omega=\frac{\pi}{2a}$ cannot happen. Then we choose $\omega=\frac{3\pi}{2a}$ to define new PEP and PEIs and find the minimum decay rate, accordingly.

Notice the terms in (3.213), the first one is the same as the PEP defined in Remark 2.1. The other terms correspond to the decay rates of the ion species when the polymer is neutral, and we may call them as principal eigenvalues of (k-th) ion (PEI or k-th PEI). The minimum decay rate of the system lies between the smallest and second smallest of PEP and PEIs. The polymer can be treated as one ion species.

For each ion species, there is a positive weight $D_kz_k^2\zeta_ke_k$ measuring how much this ion species affects the eigenvalues in (3.212). When the weight is small, the corresponding ion species has a *larger* impact on the global decay rates, this indicates ions with relatively low diffusion rate, small valence or low concentration are more important than other ones. Further more, if we decrease one weight, say $D_jz_j^2\zeta_je_j$, while fix all the others, a simple calculation shows that all the eigenvalues will move towards this PEI, $(1-\phi_0)^{-1}D_j\omega^2$. To better understand this, one may consider a system with only two ion species, and the principal eigenvalue λ_1 lies between the PEIs. Suppose at the beginning, $z_1=-z_2$ and $\zeta_1=\zeta_2$. When ion 1 diffuses very slowly, ion 2 has to wait for ion 1 to diffuse, and λ_1 is closer to the rate of ion 1; now decrease the absolute value of z_2 but maintain $z_2\zeta_2$, there are more ion 2 particles in the solution and the higher diffusion rate makes the system decay faster, just as indicated by the decrease of weight of ion 2.

What happens to λ_1 when the gel is charged from neutral state? We turn to (3.188)-(3.190). While ρ_p changes, we assume the outside concentrations, namely ζ_k, are unchanged. Differentiate w.r.t. ρ_p to derive ($\phi = \phi_0$, $\rho = \rho_p$ and $\psi = \psi_0$ with no confusion)

$$\left.\frac{d\phi}{d\rho}\right|_{\rho=0} = 0, \quad \left.\frac{d\psi}{d\rho}\right|_{\rho=0} = \frac{\frac{\phi}{1-\phi} - \frac{\rho^2}{(1-\phi)^2 f''(\phi)}}{\sum_{k=1}^N z_k^2 \zeta_k e_k} = \frac{\phi}{1-\phi} \cdot \left(\sum_{k=1}^N z_k^2 \zeta_k e_k\right)^{-1} > 0, \quad (3.214)$$

and from (3.212)

$$\left.\frac{d\lambda}{d\rho}\right|_{\rho=0}$$
$$= -\frac{\phi}{1-\phi} \cdot \sum_{k=1}^N \frac{D_k z_k^3 \zeta_k}{(1-\phi)\lambda - D_k\omega^2} \cdot \left(\sum_{k=1}^N z_k^2 \zeta_k\right)^{-1} \cdot \left(\sum_{k=1}^N \frac{D_k z_k^2 \zeta_k}{[(1-\phi)\lambda - D_k\omega^2]^2}\right)^{-1}. \quad (3.215)$$

It is easily seen that the sign of $\frac{d\lambda}{d\rho}$ only depends on

$$S := -\sum_{k=1}^N \frac{D_k z_k^3 \zeta_k}{(1-\phi)\lambda - D_k\omega^2} = -\sum_{k=1}^N z_k \cdot \frac{D_k z_k^2 \zeta_k}{(1-\phi)\lambda - D_k\omega^2}, \quad (3.216)$$

since all other terms are positive. At $\rho_p = 0$, if λ_1 is PEP, S has indefinite sign; if λ_1 is a PEI, there are two cases. Let $D_1 = \min\{D_1, \cdots, D_N\}$ and for simplicity, we assume it is unique. When $N = 2$, it is easily seen that sgn(S)=-sgn(z_1); when $N > 2$, one might guess the same conclusion holds. If $z_2, \cdots, z_N$ all have opposite signs with z_1, it is; however, in general, this is not true. Here is an example.

Let $z_1 > 0$ and $z_2 > 0$. We fix all the z_k's and ζ_k's except z_2 and ζ_2. Since they satisfy (3.189), we may increase z_2 by $z_2 \mapsto hz_2$ and $\zeta_2 \mapsto h^{-1}\zeta_2$. When h is sufficiently large, the principal eigenvalue of (3.212) satisfies $\lambda_1 \approx (1-\phi)^{-1}D_1\omega^2 + Ch^{-1}$, C independent of h. Now in S, the first term is negative and of order h, but the second term is positive and of order h^2, all other terms are bounded. $S > 0$ for sufficiently large h. This indicates z_1 cannot determine the sign of S, or $\frac{d\lambda}{d\rho}$.

The trend of λ_1 with respect to ρ_p can also be explained in terms of weights. If, at $\rho_p = 0$, λ_1 is PEP, since it is a singular point of (3.212), the direction of λ_1 depends on all other ions, and is unclear. If λ_1 is a PEI, say ion 1 has the smallest diffusion rate and $z_1 > 0$. The increase of ρ_p from 0 to positive will decrease the concentration of ion 1, hence decrease the weight of ion 1. When there are only two ion species, there is no other choice but the other ion species is anion and the concentration increases, so does the weight of ion 2. Then λ_1 is forced to move towards PEI1. When there are more than two ion species, it is still true, as ρ_p increases, PEI1 is "dragging" λ_1 with help from all anion species, however, if there exists an extremely strong cation that can overcome all these effects, then λ_1 can move in the other direction.

We provide the proof of theorem 3.5 to close this simple case.

Proof. (of theorem 3.5) Let $\psi_1 = \cos\omega(x-\alpha)$ as before, from (3.206) and (3.207) we get

$$v = \frac{\phi_0(1-\phi_0)\rho_p\omega^2}{((\kappa+(1-\phi_0)^2H\omega^2)\lambda - \phi_0^2(1-\phi_0)^2f''(\phi_0)\omega^2}\cos\omega(x-\alpha); \tag{3.217}$$

$$d_k = \frac{D_k\omega^2}{(1-\phi_0)\lambda - D_k\omega^2}\cos\omega(x-\alpha). \tag{3.218}$$

Apply the above equations to (3.208), we derive (3.212), which is of the following pattern:

$$\sum_{i=1}^{M}\frac{\alpha_i}{x-\beta_i} = 0, \quad \alpha_i, \beta_i > 0, \ \ \beta_1 < \beta_2 < \cdots < \beta_M, \tag{3.219}$$

there are $M-1$ roots each of which lies in (β_i, β_{i+1}). For (3.212), the corresponding β_i's are

$$\frac{\phi_0^2 f''(\phi_0)}{\frac{\kappa}{(1-\phi_0)^2\omega^2} + H}, \ \frac{D_k\omega^2}{1-\phi_0}, \ k = 1, \cdots, N. \tag{3.220}$$

From (3.209)-(3.210) we may derive $\omega = (n+\frac{1}{2})\frac{\pi}{a}$, $n \in \mathbb{N}\cup\{0\}$. Therefore, when $\omega = \frac{\pi}{2a}$, the smallest root λ_1 lies in (γ_1, γ_2) defined by (3.213). Finally, we need to prove this λ_1 is the smallest root of (3.212) among all possible ω. In fact, we have

$$\frac{d\lambda_1}{d\omega} > 0. \tag{3.221}$$

Consequently, the minimal decay rate is achieved when $\omega = \frac{\pi}{2a}$.

Proof of (3.221). It is convenient to write (3.212) in the form

$$\sum_{k=1}^{N} \frac{\alpha_k}{\lambda_1 - \beta_k \omega^2} + \frac{1}{(1+\alpha_0\omega^2)\lambda_1 - \beta_0\omega^2} = 0, \quad \alpha_0, \alpha_k, \beta_0, \beta_k > 0. \tag{3.222}$$

Differentiate to get

$$\begin{aligned} &\frac{d\lambda_1}{d\omega^2}\left(\sum_{k=1}^{N} \frac{\alpha_k}{(\lambda_1 - \beta_k\omega^2)^2} + \frac{1+\alpha_0\omega^2}{((1+\alpha_0\omega^2)\lambda_1 - \beta_0\omega^2)^2}\right) \\ &= \sum_{k=1}^{N} \frac{\alpha_k\beta_k}{(\lambda_1 - \beta_k\omega^2)^2} - \frac{\alpha_0\lambda_1 - \beta_0}{((1+\alpha_0\omega^2)\lambda_1 - \beta_0\omega^2)^2}. \end{aligned} \tag{3.223}$$

We need to prove the right hand side is positive, since for the left hand side, the quantity in the big bracket is positive. There are two possibilities: (i) in (3.213), the smallest is a PEI. In this case,

$$\lambda_1 < \text{PEP} \ \text{ or } \ (1+\alpha_0\omega^2)\lambda_1 - \beta_0\omega^2 < 0, \ \text{ hence } \ \alpha_0\lambda_1 - \beta_0 < 0, \tag{3.224}$$

and hence the right hand side is positive. (ii) in (3.213), the smallest is the PEP. In this case, if $\alpha_0\lambda_1 - \beta_0 < 0$, the proof is done. Otherwise,

$$\begin{aligned} &\sum_{k=1}^{N} \frac{\alpha_k\beta_k}{(\lambda_1 - \beta_k\omega^2)^2} - \frac{\alpha_0\lambda_1 - \beta_0}{((1+\alpha_0\omega^2)\lambda_1 - \beta_0\omega^2)^2} \\ &= \sum_{k=1}^{N} \frac{\alpha_k\beta_k}{(\lambda_1 - \beta_k\omega^2)^2} + \frac{\alpha_0\lambda_1 - \beta_0}{(1+\alpha_0\omega^2)\lambda_1 - \beta_0\omega^2} \cdot \frac{1}{(1+\alpha_0\omega^2)\lambda - \beta_0\omega^2} \\ &= \sum_{k=1}^{N} \frac{\alpha_k\beta_k}{(\lambda_1 - \beta_k\omega^2)^2} + \frac{\alpha_0\lambda_1 - \beta_0}{((1+\alpha_0\omega^2)\lambda_1 - \beta_0\omega^2)} \cdot \sum_{k=1}^{N} \frac{\alpha_k}{\lambda_1 - \beta_k\omega^2} \\ &= \sum_{k=1}^{N} \frac{\alpha_k}{\lambda_1 - \beta_k\omega^2}\left(\frac{\beta_k}{\lambda_1 - \beta_k\omega^2} + \frac{\alpha_0\lambda_1 - \beta_0}{(1+\alpha_0\omega^2)\lambda_1 - \beta_0\omega^2}\right) \end{aligned} \tag{3.225}$$

Now, since $\lambda_1 < \beta_k$ for all k, and $\alpha_0\lambda_1 - \beta_0 > 0$,

$$\frac{\beta_k}{\lambda_1 - \beta_k\omega^2} + \frac{\alpha_0\lambda_1 - \beta_0}{\lambda_1 + \alpha_0\omega^2\lambda_1 - \beta_0\omega^2} < \frac{\beta_k}{0 - \beta_k\omega^2} + \frac{\alpha_0\lambda_1 - \beta_0}{0 + \alpha_0\omega^2\lambda_1 - \beta_0\omega^2} = 0, \tag{3.226}$$

which means for each k, the product is positive, hence $\frac{d\lambda_1}{d\omega^2} > 0$, and the conclusion follows. $\square$

3.4.3 Minimum decay rate: a more general case

Let $\mathbb{U} = (0, L)$, $\Omega = (0, a)$ and the gel be fixed at $x = 0$. We turn to a more general case when there are two ion species and the diffusion coefficients $D_{1,2}$ are both constants in $(0, L)$. The perturbation variables $\{u, d_k, \psi_1\}$ are determined by (‡). Let

$$u(x,t) = e^{-\lambda t}\widetilde{u}(x), \quad \psi_1(x,t) = e^{-\lambda t}\widetilde{\psi_1}(x), \quad d_k = e^{-\lambda t}\widetilde{d}_k(x), \tag{3.227}$$

and we derive the following system in $(0, L)$:

At $x = 0$,

$$u = 0, \ \ (d_k^+ + \psi_1^+)_x = 0; \tag{3.228}$$

and in $(0, a)$,

$$(-\lambda H + \phi_0^2 f''(\phi_0))u_{xx} = -\frac{\kappa\lambda}{(1-\phi_0)^2}u + \frac{\phi_0\rho_p}{1-\phi_0}(\psi_1^+)_x; \tag{3.229}$$

$$-\lambda d_k^+ = \frac{D_k^+}{1-\phi_0}\left(d_k^+ + \psi_1^+\right)_{xx}, \ \ D_k^+ = D_k^+(\phi_0); \tag{3.230}$$

$$\sum_{k=1}^{N} z_k^2 \zeta_k e_k^+ d_k^+ = \frac{\phi_0\rho_p}{(1-\phi_0)^2}u_x \tag{3.231}$$

while at $x = a$:

$$\lambda u(e_k^+ - e_k^-) = z_k\left[D_k e_k\left(d_k + \psi_1\right)_x\right]; \tag{3.232}$$

$$[d_k + \psi_1] = 0; \tag{3.233}$$

$$\lambda\eta_\perp u = (-\lambda H + \phi_0^2 f''(\phi_0))u_x - \sum_{k=1}^{N} z_k\zeta_k\left[e_k d_k\right] \quad \text{at } \ x = a; \tag{3.234}$$

and in (a, L),

$$-\lambda d_k^- = D_k^-(d_k^- + \psi_1^-)_{xx}; \tag{3.235}$$

$$\sum_{k=1}^{N} z_k^2 \zeta_k e_k^- d_k^- = 0 \tag{3.236}$$

while at $x = L$:

$$(d_k^- + \psi_1^-)_x = 0, \tag{3.237}$$

in which we have dropped the tildes for notational convenience. We further assume $\eta_\perp = 0$ and temporarily let

$$H = 0, \tag{3.238}$$

and consider the case when there are only two ion species, namely $k = 2$. Let $z_1 > 0$ and $z_2 < 0$. Then (3.229)-(3.231) become

$$-\lambda u = A_1 u_{xx} + A_2(\psi_1^+)_x; \tag{3.239}$$

$$-\lambda d_k^+ = B_k(d_k^+)_{xx} + B_k(\psi_1^+)_{xx}, \;\; k = 1, 2; \tag{3.240}$$

$$C_1 d_1^+ + C_2 d_2^+ = -u_x := w; \tag{3.241}$$

in which

$$A_1 = \frac{f''(\phi_0)\phi_0^2(1-\phi_0)^2}{\kappa}, \;\; A_2 = -\frac{\rho_p\phi_0(1-\phi_0)}{\kappa}; \tag{3.242}$$

$$B_k = \frac{D_k^+}{1-\phi_0}, \;\; C_k = -\frac{z_k^2\zeta_k e_k^+(1-\phi_0)^2}{\phi_0\rho_p}; \tag{3.243}$$

$$A_{1,2}, \;\; B_{1,2}, \;\; C_{1,2} > 0. \tag{3.244}$$

Recall (3.189) and (3.190), let

$$\zeta = z_1\zeta_1 = -z_2\zeta_2, \tag{3.245}$$

and consequently

$$C_1 = \frac{z_1 e_1^+(1-\phi_0)}{e_1^+ - e_2^+}, \quad C_2 = -\frac{z_2 e_2^+(1-\phi_0)}{e_1^+ - e_2^+}. \tag{3.246}$$

Remark 3.3. *Looking at the linearized momentum equation* (3.229)*, the polymer phase satisfies a diffusion-type equation. Experimental data shows that* $\lambda H \ll \phi_0^2 f''(\phi_0)$ *and the diffusion coefficient* A_1 *as in* (3.239) *is much smaller than ionic diffusion coefficients* D_k *(see, such as [A multiphasic model for the volume change of polyelectrolyte hydrogels]). The linearization indicates near the equilibrium, the gel's swelling behavior is similar to a slow diffusive ion species.*

Differentiate (3.239) and add (3.240)(k=1,2) multiplied by C_k, use (3.241) to get

$$(A_2 + B_1C_1 + B_2C_2)(\psi_1^+)_{xx} - A_1 w_{xx} + B_1C_1(d_1^+)_{xx} + B_2C_2(d_2^+)_{xx} = 0, \tag{3.247}$$

then integrate and use the boundary conditions to derive

$$\begin{aligned}(\psi_1^+)_x &= \frac{A_1 w_x - B_1C_1(d_1^+)_x - B_2C_2(d_2^+)_x}{A_2 + B_1C_1 + B_2C_2} \\ &= \frac{(A_1 - B_1)C_1}{A_2 + B_1C_1 + B_2C_2}(d_1^+)_x + \frac{(A_1 - B_2)C_2}{A_2 + B_1C_1 + B_2C_2}(d_2^+)_x\end{aligned} \tag{3.248}$$

from (3.228) and (3.241). Now apply (3.248) to (3.239)-(3.241), to derive

$$-\lambda \begin{bmatrix} d_1^+ \\ d_2^+ \end{bmatrix} = \begin{bmatrix} p & q \\ r & s \end{bmatrix} \cdot \frac{d^2}{dx^2} \begin{bmatrix} d_1^+ \\ d_2^+ \end{bmatrix} \quad \text{or} \quad \frac{d^2}{dx^2} \begin{bmatrix} d_1^+ \\ d_2^+ \end{bmatrix} = \frac{\lambda}{ps - rq} \begin{bmatrix} -s & q \\ r & -p \end{bmatrix} \begin{bmatrix} d_1^+ \\ d_2^+ \end{bmatrix} \tag{3.249}$$

in which

$$\begin{aligned} p &= \frac{B_1(A_2 + B_2C_2 + A_1C_1)}{A_2 + B_1C_1 + B_2C_2}, \quad q = \frac{B_1(A_1 - B_2)C_2}{A_2 + B_1C_1 + B_2C_2}, \\ r &= \frac{B_2(A_1 - B_1)C_1}{A_2 + B_1C_1 + B_2C_2}, \quad s = \frac{B_2(A_2 + B_1C_1 + A_1C_2)}{A_2 + B_1C_1 + B_2C_2}. \end{aligned} \tag{3.250}$$

We need the following lemmas first.

Lemma 3.2. *The determinant $ps - rq > 0$.*

Proof. A direct computation yields

$$\begin{aligned}(ps - rq)(A_2 + B_1C_1 + B_2C_2)^2(B_1B_2)^{-1} = A_2^2 + A_2B_2C_2 + A_1A_2C_1 + A_2B_1C_1 \\ + A_1B_1C_1^2 + A_1A_2C_2 + A_1B_2C_2^2 + A_1B_2C_1C_2 + A_1B_1C_1C_2 > 0\end{aligned} \tag{3.251}$$

since every term is positive. □

Lemma 3.3. *Let $\Delta = (p - s)^2 + 4rq$, then $\Delta \geq 0$.*

Proof. It suffices to prove

$$\begin{aligned}\Delta' =& (B_1A_2 + B_1B_2C_2 + B_1A_1C_1 - B_2A_2 - B_2B_1C_1 - B_2A_1C_2)^2 \\ &+ 4B_1B_2C_1C_2(B_1 - A_1)(B_2 - A_1) > 0.\end{aligned} \tag{3.252}$$

If $A_1 > \max\{B_1, B_2\}$ or $A_1 < \min\{B_1, B_2\}$, obviously $\Delta' > 0$. Now assume A_1 lies in between B_1 and B_2.

$$\frac{\partial \Delta'}{\partial A_2} = 2(B_1 - B_2)(B_1A_2 - B_2A_2 + B_1B_2C_2 + B_1A_1C_1 - B_2B_1C_1 - B_2A_1C_2), \quad (3.253)$$

if $\frac{\partial \Delta'}{\partial A_2} = 0$, then

$$A_2 = \frac{(A_1 - B_1)B_2C_2 + (B_2 - A_1)B_1C_1}{B_1 - B_2} < 0 \quad (3.254)$$

hence Δ' is monotone in A_2 for $A_2 \geq 0$. On the other hand,

$$\Delta'(A_2 = 0) = (B_1C_1(B_2 - A_1) + B_2C_2(B_1 - A_1))^2 > 0, \quad (3.255)$$

$$\Delta'(A_2 = \infty) = (B_1 - B_2)^2 \cdot \infty = \infty, \quad (3.256)$$

which indicates $\Delta' > 0$ for all $A_2 > 0$. □

Now it is clear that the eigenvalues of (3.249) can be expressed by $\omega_1^2\lambda, \omega_2^2\lambda$, and $\omega_1 > \omega_2 > 0$ satisfy

$$(ps - rq)\omega^4 - (p + s)\omega^2 + 1 = 0. \quad (3.257)$$

They are given by

$$\omega_1^2 := \frac{p + s + \sqrt{(p - s)^2 + 4rq}}{2(ps - rq)}, \ \ \omega_2^2 := \frac{p + s - \sqrt{(p - s)^2 + 4rq}}{2(ps - rq)} \quad (3.258)$$

We consider the generic situation that $A_1 \neq B_1, B_2$, from (3.249) we have

$$rq \neq 0. \quad (3.259)$$

The equal case is much simpler and will be mentioned later when necessary. From the boundary conditions (3.228) and (3.248), $(d_k^+)_x = 0$ at $x = 0$. Therefore, d_1^+ and d_2^+ are linear combinations of $\cos(\omega_1 x)$ and $\cos(\omega_2 x)$, and

$$\begin{bmatrix} d_1^+ \\ d_2^+ \end{bmatrix} = \begin{bmatrix} 1 - s\omega_1^2 \\ r\omega_1^2 \end{bmatrix} \alpha \cos(\omega_1 \sqrt{\lambda} x) + \begin{bmatrix} q\omega_2^2 \\ 1 - p\omega_2^2 \end{bmatrix} \beta \cos(\omega_2 \sqrt{\lambda} x). \quad (3.260)$$

We turn to (3.235)-(3.237). Without loss of generality, let $\psi_0^- = 0$ and we have

$$e_1^- = e_2^- = 1. \tag{3.261}$$

A similar calculation in (a, L) reveals

$$(\psi_1^-)_{xx} = \frac{z_1(D_2^- - D_1^-)}{z_1 D_1^- - z_2 D_2^-}(d_1^-)_{xx}, \quad d_2^- = \frac{z_1}{z_2} d_1^-. \tag{3.262}$$

Apply (3.262) to (3.237) to derive $(d_1^-)_x = 0$ at $x = L$. Therefore, we may let

$$d_1^- = \gamma \cos(\omega \sqrt{\lambda}(x - L)), \quad \omega = \sqrt{\frac{(z_1 D_1^- - z_2 D_2^-)}{(z_1 - z_2) D_1^- D_2^-}}. \tag{3.263}$$

We turn to boundary conditions (3.232)-(3.234). Use (3.239) to get

$$\begin{aligned}\lambda u &= A_1 w_x - A_2(\psi_1^+)_x \\ &= \frac{A_1 B_1 C_1 + A_1 B_2 C_2 + A_2 B_1}{A_2 + B_1 C_1 + B_2 C_2} C_1 (d_1^+)_x + \frac{A_1 B_1 C_1 + A_1 B_2 C_2 + A_2 B_2}{A_2 + B_1 C_1 + B_2 C_2} C_2 (d_2^+)_x,\end{aligned} \tag{3.264}$$

and from (3.248), it follows (3.232)($k = 1$) becomes

$$\begin{aligned}&\left(\left(A_1 C_1 - \frac{A_2 r}{B_2}\right)(d_1^+)_x + \left(A_1 C_2 - \frac{A_2 q}{B_1}\right)(d_2^+)_x\right)(e_1^+ - 1) \\ =& z_1 \left(D_1^+ e_1^+ \left(1 + \frac{r}{B_2}\right)(d_1^+)_x + D_1^+ e_1^+ \left(\frac{q}{B_1}\right)(d_2^+)_x - \omega^{-2}(d_1^-)_x\right).\end{aligned} \tag{3.265}$$

(3.232)($k = 2$) is derived when (3.265) is multiplied by z_2/z_1, hence they are equivalent. For (3.233), we may choose suitable $[\psi_1]$, such that it reduces to

$$[d_1] = [d_2] \quad \Longleftrightarrow \quad d_1^+ - d_2^+ = -\frac{z_1 - z_2}{z_2} d_1^-. \tag{3.266}$$

Finally, (3.234) becomes

$$(e_1^+ + \phi_0^2 f''(\phi_0) C_1 \zeta^{-1}) d_1^+ + (-e_2^+ + \phi_0^2 f''(\phi_0) C_2 \zeta^{-1}) d_2^+ = -\frac{z_1 - z_2}{z_2} d_1^-, \tag{3.267}$$

here (3.245) is used. (3.266) and (3.267) cannot be equivalent, since

$$\begin{aligned}&\zeta e_1^+ + \phi_0^2 f''(\phi_0)C_1 - \zeta e_2^+ + \phi_0^2 f''(\phi_0)C_2\\ =&\phi_0^2 f''(\phi_0)(C_1+C_2) + \zeta(e_1^+ - e_2^+) > 0,\end{aligned} \tag{3.268}$$

all the terms are positive with $e_1^+ > 1 > e_2^+$.

Now the system (3.228)-(3.237) is reduced to (3.265)-(3.267) in which $\{d_1^+, d_2^+, d_1^-\}$ are defined by (3.260) and (3.263). There are four unknowns $\{\alpha, \beta, \gamma, \lambda\}$, but $\lambda^* > 0$ is called an eigenvalue only if the linear system for $\{\alpha, \beta, \gamma\}$ has nontrivial solutions when $\lambda = \lambda^*$. We rewrite (3.265)-(3.267) in the matrix form:

$$\begin{bmatrix} a_{11}\cos(\omega_1\sqrt{\lambda}a) & a_{12}\cos(\omega_2\sqrt{\lambda}a) & \frac{z_1-z_2}{z_2}\cos(\omega\sqrt{\lambda}(L-a)) \\ a_{21}\cos(\omega_1\sqrt{\lambda}a) & a_{22}\cos(\omega_2\sqrt{\lambda}a) & \frac{z_1-z_2}{z_2}\cos(\omega\sqrt{\lambda}(L-a)) \\ a_{31}\omega_1\sin(\omega_1\sqrt{\lambda}a) & a_{32}\omega_2\sin(\omega_2\sqrt{\lambda}a) & z_1\omega^{-1}\sin(\omega\sqrt{\lambda}(L-a)) \end{bmatrix} \begin{bmatrix}\alpha\\ \beta\\ \gamma\end{bmatrix} = 0. \tag{3.269}$$

in which

$$a_{11} = 1-(s+r)\omega_1^2, \quad a_{12} = (p+q)\omega_2^2 - 1, \tag{3.270}$$

$$a_{21} = (e_1^+ + \phi_0^2 f''(\phi_0)C_1\zeta^{-1})(1-s\omega_1^2) + (-e_2^+ + \phi_0^2 f''(\phi_0)C_2\zeta^{-1})(r\omega_1^2), \tag{3.271}$$

$$a_{22} = (e_1^+ + \phi_0^2 f''(\phi_0)C_1\zeta^{-1})(q\omega_2^2) + (-e_2^+ + \phi_0^2 f''(\phi_0)C_2\zeta^{-1})(1-p\omega_2^2), \tag{3.272}$$

and we simplify a_{31} and a_{32} in the following manner. (3.265) can be written as

$$M_1(d_1^+)_x + M_2(d_2^+)_x + z_1\omega^{-2}(d_1^-)_x = 0, \tag{3.273}$$

$$\begin{aligned} M_1 &= \frac{A_1B_1C_1 + A_1B_2C_2 + A_2B_1}{A_2 + B_1C_1 + B_2C_2}\cdot C_1(e_1^+ - 1) - \frac{A_2 + B_2C_2 + A_1C_1}{A_2 + B_1C_1 + B_2C_2}\cdot z_1 D_1^+ e_1^+ \\ &= (pC_1 + rC_2)(e_1^+ - 1) - (pB_1^{-1})\cdot z_1 D_1^+ e_1^+ \\ &= (1-\phi_0)\left(-z_1 e_1^+ p\cdot\frac{1-e_2^+}{e_1^+ - e_2^+} - z_2 e_2^+ r\cdot\frac{e_1^+ - 1}{e_1^+ - e_2^+}\right) \\ &= (1-\phi_0)\left(-z_1 e_1^+ p\tau - z_2 e_2^+ r(1-\tau)\right), \quad \tau = \frac{1-e_2^+}{e_1^+ - e_2^+} \in (0,1), \end{aligned} \tag{3.274}$$

$$
\begin{aligned}
M_2 &= \frac{A_1B_1C_1 + A_1B_2C_2 + A_2B_2}{A_2 + B_1C_1 + B_2C_2} \cdot C_2(e_1^+ - 1) - \frac{(A_1 - B_2)C_2}{A_2 + B_1C_1 + B_2C_2} \cdot z_1 D_1^+ e_1^+ \\
&= (sC_2 + qC_1)(e_1^+ - 1) - (qB_1^{-1}) \cdot z_1 D_1^+ e_1^+ \\
&= (1 - \phi_0) \left(-z_1 e_1^+ q \cdot \frac{1 - e_2^+}{e_1^+ - e_2^+} - z_2 e_2^+ s \cdot \frac{e_1^+ - 1}{e_1^+ - e_2^+} \right) \\
&= (1 - \phi_0) \left(-z_1 e_1^+ q\tau - z_2 e_2^+ s(1 - \tau) \right) .
\end{aligned}
\tag{3.275}
$$

The above calculation implies

$$
\begin{aligned}
a_{31} =& - M_1(1 - s\omega_1^2) - M_2(r\omega_1^2) \\
=&(1 - \phi_0) \left(z_1 e_1^+ \tau(p - (ps - rq)\omega_1^2) + z_2 e_2^+ (1 - \tau) r \right) ; \\
a_{32} =& - M_1(q\omega_2^2) - M_2(1 - p\omega_2^2) \\
=&(1 - \phi_0) \left(z_1 e_1^+ \tau q + z_2 e_2^+ (1 - \tau)(s - (ps - rq)\omega_2^2) \right) .
\end{aligned}
$$

We have derived and simplified the matrix from which the eigenvalues λ's are implicitly determined when the determinant of the matrix is zero. A natural question arises as, can we find some upper or lower bound for the principle eigenvalue λ_1 from this very complicated expression, in terms of PEP and PEIs? In general, it is not likely; however, as Remark 3.3 says, we may assume

$$
A_1 < B_1, B_2. \tag{3.276}
$$

Under this condition, we have the following results.

Consider the upper bound first. If all the cosine functions are nonzero, we may write the equation for λ as a linear combination of three tangent functions $\tan(\omega_1\sqrt{\lambda}a)$, $\tan(\omega_2\sqrt{\lambda}a)$ and $\tan(\omega\sqrt{\lambda}(L-a))$. Notice that λ does not appear in the coefficients, there must be at least one solution when the largest angle lies in $(0, 3\pi/2)$. Consequently, we have

$$
\max\{\omega_1\sqrt{\lambda_1}a, \omega\sqrt{\lambda_1}(L-a)\} < \frac{3\pi}{2} \quad \text{or} \quad \lambda < \frac{3\pi}{2} \cdot \min\left\{(a\omega_1)^{-2}, ((L-a)\omega)^{-2}\right\} . \tag{3.277}
$$

The expression of ω is given in (3.263), we need to estimate ω_1. It can be seen from the quadratic form that

$$\begin{aligned} u^2-(p+s)u+(ps-rq)\le 0 \quad &\Rightarrow \quad \omega_1^2 \ge \frac{1}{u} \ge \omega_2^2, \\ \text{in particular,} \quad &\omega_1^2 \ge \frac{1}{p}, \ \ \frac{1}{s} \ge \omega_2^2, \end{aligned} \tag{3.278}$$

since $r, q < 0$ from (3.276). Again, from (3.276), $p < B_1$, $s < B_2$, we have

$$\lambda_1 < \left(\frac{3\pi}{2}\right)^2 \cdot \min\left\{\frac{B_1}{a^2},\ \frac{B_2}{a^2},\ \frac{(z_1-z_2)D_1^-D_2^-}{(L-a)^2(z_1D_1^- - z_2D_2^-)}\right\}. \tag{3.279}$$

This estimate includes the situation when any cosine function vanishes, hence it comes along with (3.276).

Now consider the lower bound. We assume all of the cosine functions are nonzero, it will be seen later the estimate includes the zero case. Again, we write the equation for λ as a linear combination of tangent functions. If all the coefficients are positive (or negative), then there is no solution when the largest angle lies in $(0, \pi/2)$. In the following, we present some technical computation to show this is true, when $z_1 \le -z_2$ and $D_1 \le D_2$.

We turn to the 3-by-3 matrix in (3.269). Divide each column by the corresponding cosine function, subtract the first row from the second row, and divide the second row by $(e_1^+ - e_2^+) + \phi_0^2 f''(\phi_0)(C_1+C_2)\zeta^{-1}$. Let

$$\chi = e_1^+ - 1 + \phi_0^2 f''(\phi_0) C_1 \zeta^{-1}, \quad \chi \in (0,1), \tag{3.280}$$

the matrix can be written as $M =$

$$\begin{bmatrix} 1-(s+r)\omega_1^2 & (p+q)\omega_2^2 - 1 & \frac{z_1-z_2}{z_2} \\ \chi(1-s\omega_1^2)+(1-\chi)(r\omega_1^2) & \chi(q\omega_2^2)+(1-\chi)(1-p\omega_2^2) & 0 \\ a_{31}\omega_1\tan(\omega_1\sqrt{\lambda}a) & a_{32}\omega_1\tan(\omega_2\sqrt{\lambda}a) & \frac{z_1}{\omega}\tan(\omega\sqrt{\lambda}(L-a)) \end{bmatrix}, \tag{3.281}$$

$$a_{31} = (1-\phi_0)\left(z_1e_1^+\tau(p-(ps-rq)\omega_1^2) + z_2e_2^+(1-\tau)r\right); \tag{3.282}$$

$$a_{32} = (1-\phi_0)\left(z_1e_1^+\tau q + z_2e_2^+(1-\tau)(s-(ps-rq)\omega_2^2)\right). \tag{3.283}$$

and we denote

$$\det(M) = K_1 \tan(\omega_1\sqrt{\lambda}a) + K_2 \tan(\omega_2\sqrt{\lambda}a) + K_3 \tan(\omega\sqrt{\lambda}(L-a)). \tag{3.284}$$

From here, the calculation is divided into several steps: (1) $K_2, K_3 < 0$; (2) Let $z_1 = -z_2$, show $M_{22} = \chi(q\omega_2^2) + (1-\chi)(1-p\omega_2^2) > 0$; (3) $a_{31} < 0$ hence $K_1 < 0$; (4) calculation of (2)-(3) when $z_1 < -z_2$.

Proof of (1). We use M_{ij} to represent entries of M. Recall $z_1 > 0 > z_2$, $e_1^+ > 1 > e_2^+$, $\chi, \tau \in (0,1)$ and $p, s > 0$, $r, q < 0$, from (3.278) and

$$s - (ps - rq)\omega_2^2 = \frac{(s-p) - \sqrt{(s-p)^2 + 4rq}}{2} < 0, \tag{3.285}$$

it follows $M_{21} < 0$ and $a_{32} < 0$. Therefore, $K_2 < 0$. With some calculation,

$$M_{11}M_{22} - M_{21}M_{12} = (1 - s\omega_1^2)(1 - p\omega_2^2) - rq\omega_1^2\omega_2^2 < 0, \tag{3.286}$$

and we get $K_3 < 0$.

Proof of (2). Let $z_1 = -z_2 = z > 0$, for convenience denote

$$\begin{aligned}
&x = e_1^+ > 1, \quad A_2 = \frac{1}{1-\phi_0} \cdot \frac{z}{x - \frac{1}{x}} \cdot A_2', \\
&p = \frac{B_1(A_1 x + A_2' + B_2/x)}{B_1 x + A_2' + B_2/x}, \quad q = -\frac{B_1(B_2 - A_1)/x}{B_1 x + A_2' + B_2/x}, \\
&r = -\frac{B_2(B_1 - A_1)x}{B_1 x + A_2' + B_2/x}, \quad s = \frac{B_2(B_1 x + A_2' + A_1/x)}{B_1 x + A_2' + B_2/x}.
\end{aligned} \tag{3.287}$$

From (3.287),

$$\begin{aligned}
\chi &= x - 1 + \phi_0^2(1-\phi_0)f''(\phi_0)z\zeta^{-1} \cdot \frac{x}{x - \frac{1}{x}} \\
&< x^2 \cdot \left(1 - \frac{1}{x} + \phi_0^2(1-\phi_0)f''(\phi_0)z\zeta^{-1} \cdot \frac{\frac{1}{x}}{x - \frac{1}{x}}\right) = x^2(1-\chi),
\end{aligned} \tag{3.288}$$

and then

$$\begin{aligned}
M_{22} =& \chi(q\omega_2^2) + (1-\chi)(1-p\omega_2^2) \\
>& (1-\chi)(x^2 q\omega_2^2 + 1 - p\omega_2^2) = (1-\chi)\left(1 - (p - x^2 q)\omega_2^2\right).
\end{aligned} \tag{3.289}$$

Let $u = p - x^2 q$ in (3.278), with some calculation,

$$u^2 - u(p+s) + ps - rq = -q(x^2 p - x^4 q - x^2 s + r) = -q \cdot \frac{(B_1 - B_2)A_2' x^2}{B_1 x + A_2' + B_2/x} < 0, \quad (3.290)$$

which indicates $M_{22} > 0$ in (3.289).

Proof of (3). First, we have

$$s - p = \frac{B_1(B_2 - A_1)x + (B_2 - B_1)A_2' + B_2(A_1 - B_1)/x}{A_2 + B_1 C_1 + B_2 C_2} \quad (3.291)$$

the numerator is an increasing function and positive for $x = 1$, hence $s > p$. Now,

$$\begin{aligned} a_{31} &= (1 - \phi_0)\left(z_1 e_1^+ \tau (p - (ps - rq)\omega_1^2) + z_2 e_2^+ (1 - \tau) r\right) \\ &= (1 - \phi_0) \frac{z(x-1)}{x - \frac{1}{x}} \left(-\frac{(s-p) + \sqrt{(s-p)^2 + 4rq}}{2} - \frac{r}{x} \right) \\ &< (1 - \phi_0) \frac{z(x-1)}{x - \frac{1}{x}} \left(-\sqrt{rq} - \frac{r}{x} \right) < 0, \quad \text{since} \quad -x^2 q > -r. \end{aligned}$$

Consequently, $a_{31} < 0$ and $K_1 < 0$.

Proof of (4). Let $z_2 = -h z_1$, $h > 1$ and $e_2^+ = x^{-h}$. The calculation is similar: (3.288) becomes $\chi < x^{1+h}(1 - \chi)$ and (2) follows. For (3), $s > p$ and

$$\begin{aligned} a_{31} &\sim -(x - x^{1-h}) \cdot \frac{(s-p) + \sqrt{(s-p)^2 + 4rq}}{2} - h x^{1-h}(x - 1) \cdot \frac{r}{x} \\ &< -(x - x^{1-h}) \cdot \sqrt{rq} - h(x^{2-h} - x^{1-h}) \cdot \frac{r}{x} \end{aligned}$$

Notice that $\sqrt{rq} > x^{\frac{1-h}{2}}(-\frac{r}{x})$, it suffices to prove (by multiplying some power of x)

$$x^{\frac{1+h}{2}} - x^{\frac{1-h}{2}} - x + 1 > 0. \quad (3.292)$$

This is an convex function in x for $x > 1$ and is increasing at $x = 1$, hence the inequality holds and (3) follows.

Now we have shown $K_{1,2,3} < 0$ in (3.284), and thus

$$\lambda_1 \geq \frac{\pi^2}{4} \cdot \min\left\{ \frac{1}{\omega_1^2 a^2}, \ \frac{1}{\omega^2 (L - a)^2} \right\}. \quad (3.293)$$

The equality occurs when some cosine functions in (3.269) take zero value. Furthermore,

$$\begin{aligned}
(p-A_1)(s-A_1) &= \frac{(B_1-A_1)(B_2-A_1)(A_2+B_1C_1)(A_2+B_2C_2)}{(A_2+B_1C_1+B_2C_2)^2}\\
&> \frac{(B_1-A_1)(B_2-A_1)B_1B_2C_1C_2}{(A_2+B_1C_1+B_2C_2)^2} = rq,\\
\Rightarrow ps-rq &> A_1(p+s-A_1) > A_1\cdot\frac{p+s}{2} \ \text{ or } \ \frac{ps-rq}{A_1}-\frac{p+s}{2}>0,\\
\Rightarrow \omega_1^2 &= \frac{p+s+\sqrt{(p-s)^2+4rq}}{2(ps-rq)} < \frac{1}{A_1}.
\end{aligned}$$

Therefore, from (3.293) we derive

$$\lambda_1 \geq \frac{\pi^2}{4}\cdot\min\left\{\frac{A_1}{a^2},\ \ \frac{(z_1-z_2)D_1^-D_2^-}{(z_1D_1^- - z_2D_2^-)(L-a)^2}\right\}. \tag{3.294}$$

In the above calculation, it is assumed $H=0$ in (3.238). Actually, this condition is not necessary, since H only appears in A_1 and we only used the property $A_1>0$. Now assume $H\neq 0$, there are two possibilities. If

$$A_1 = \frac{(1-\phi_0)^2(-\lambda H+\phi_0^2 f''(\phi_0))}{\kappa} > 0, \tag{3.295}$$

(3.294) remains valid, and A_1 is replaced by (3.295), we have

$$\lambda \geq \min\left\{\frac{\phi_0^2 f''(\phi_0)}{\frac{4a^2\kappa}{\pi^2(1-\phi_0)^2}+H},\ \ \frac{\pi^2}{4(L-a)^2}\cdot\frac{(z_1-z_2)D_1^-D_2^-}{(z_1D_1^- - z_2D_2^-)}\right\}, \tag{3.296}$$

and upper bound estimate (3.279). If (3.295) is not true, then

$$A_1 = \frac{(1-\phi_0)^2(-\lambda H+\phi_0^2 f''(\phi_0))}{\kappa} < 0, \ \text{ hence } \ \lambda > \frac{\phi_0^2 f''(\phi_0)}{H}. \tag{3.297}$$

This inequality is stronger than (3.296), therefore we still get (3.296).

We summarize by the following theorem.

Theorem 3.6. *Let* $\{u, d_{1,2}, \psi_1\}$ *be perturbation variables from an equilibrium state defined by* (3.175), *and they satisfy* (3.227)-(3.237). *Let* λ_1 *be the minimum decay* *rate in* (3.227)*. Assume* $-z_2 \geq z_1 > 0$ *and*

$$\frac{f''(\phi_0)\phi_0^2(1-\phi_0)^2}{\kappa} \leq \frac{D_1}{1-\phi_0} < \frac{D_2}{1-\phi_0}, \tag{3.298}$$

then

$$\begin{aligned} &\left(\frac{3\pi}{2}\right)^2 \cdot \min\left\{\frac{D_1}{a^2(1-\phi_0)}, \frac{(z_1-z_2)D_1^- D_2^-}{(L-a)^2(z_1 D_1^- - z_2 D_2^-)}\right\} \\ >&\lambda \geq \min\left\{\frac{\phi_0^2 f''(\phi_0)}{\frac{4a^2\kappa}{\pi^2(1-\phi_0)^2}+H}, \frac{\pi^2}{4(L-a)^2}\cdot\frac{(z_1-z_2)D_1^- D_2^-}{(z_1 D_1^- - z_2 D_2^-)}\right\}, \end{aligned} \tag{3.299}$$

Proof. When the equality holds in (3.298), due to $p < s$ (3.260) is still valid, and the computation thereafter is the same or simpler. □

The upper bound estimate is less restrictive that it does not require $-z_2 \geq z_1$ or $D_1 < D_2$.

In the above principal eigenvalue analysis, we considered the three components of the system: gel, inside ions and outside ions. Their intrinsic decay rates are closed related to the mixture. Theorem 3.6 states that under certain conditions, the global decay rate must be faster than the slowest component in the system. We propose, but cannot prove this estimate holds for the general case.

3.5 Computational demonstration

We have developed a numerical method to simulate the one-dimensional model with ion species. There are several difficulties in developing a numerical scheme for this problem. This is a moving interface problem. We write all of our equations in the reference configuration and discretize the resulting equations on a moving Lagrangian grid. The ion concentration equations are discretized so that the total amount of each ion is conserved. We use the backward Euler scheme for time-stepping. This is necessitated in part by the presence of the algebraic constraint of electroneutrality. The resulting nonlinear system of equations is solved using Newton's method. To alleviate the difficulty of finding a good initial guess for Newton's method at the first time step, we start from a steady state solution and iterate along a homotopy path to the current initial data. The details of this numerical scheme can be found in the appendix II. Here, we demonstrate some representative computational results and numerically verify the stability calculations of the previous section.

The following figures show the evolution of ϕ_1, ψ, c_1, c_2 at $t = 0, 0.1, 1, 10$, with

$$L = 5,\ a = 3,\ \eta_1 = 0.01,\ \eta_2 = 0.02,\ \eta_\perp = 0,\ \kappa = 1,\ \rho_p = -0.5,$$
$$z_1 = 1,\ z_2 = -1,\ D_1^- = 2,\ D_2^- = 4,\ D_{1,2}^+ = (1-\phi)D_{1,2}^-,\ f(\phi) = \frac{1}{\phi(1.2-\phi)}$$

and initial conditions

$$\begin{aligned} \phi_1 = 0.7, \quad c_1 &= 2.49 + 0.05 \cdot \sin x \qquad \text{for } 0 < x < 3; \\ c_1 &= 0.27 + 0.05 \cdot x \qquad \text{for } 3 < x < 5. \end{aligned}$$

Remark 3.4. *The diffusion coefficient of polymer,* $A_1 = \frac{f''(\phi_0)\phi_0^2(1-\phi_0)^2}{\kappa} = 0.772$ *is smaller than* $B_1 = 2$ *and* $B_2 = 4$*. This is in accordance with data from [].*

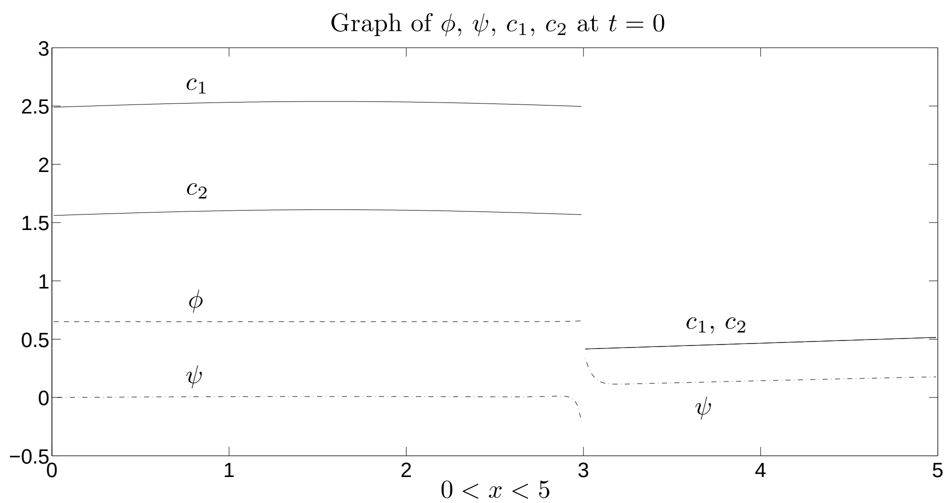

Figure 3.1: Graph of ϕ, ψ, c_1, c_2 at $t = 0$

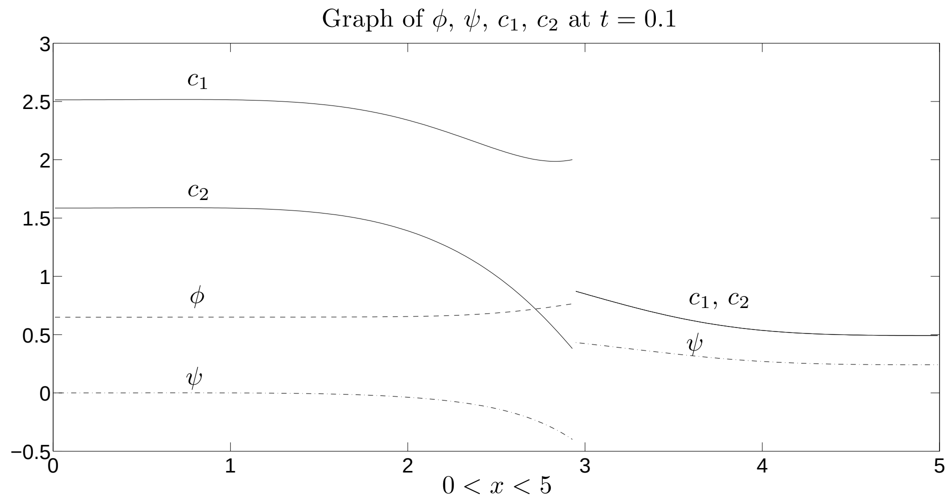

Figure 3.2: Graph of ϕ, ψ, c_1, c_2 at $t = 0.1$

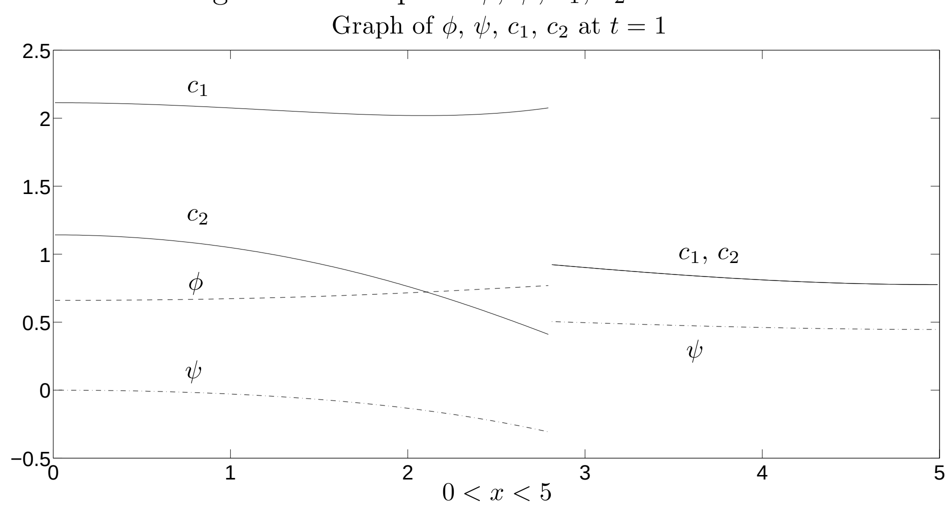

Figure 3.3: Graph of ϕ, ψ, c_1, c_2 at $t = 1$

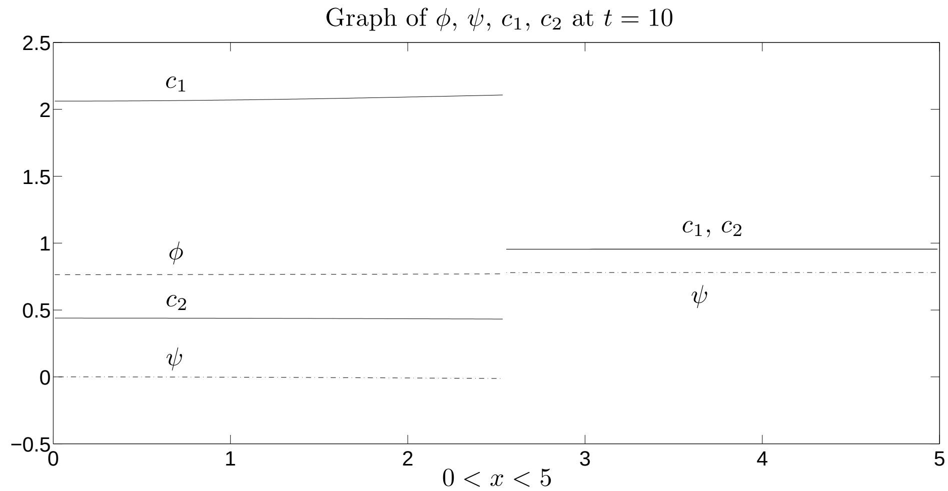

Figure 3.4: Graph of ϕ, ψ, c_1, c_2 at $t = 10$

In the vicinity of $t = 0$, the interface is moving fast towards the steady state direction, and ϕ_1 approaches ϕ_0 faster near $x = a(t)$. Consequently, at the beginning of the transient state, the variables c_k, ψ are moving rapidly near the interface, and an edge forms for the concentrations. The graphs gradually flatten out and get close to the steady state solution. The following figure shows the curve of $c_1(x, t)$ for $0 < x < a(t)$, $0 < t < 1$.

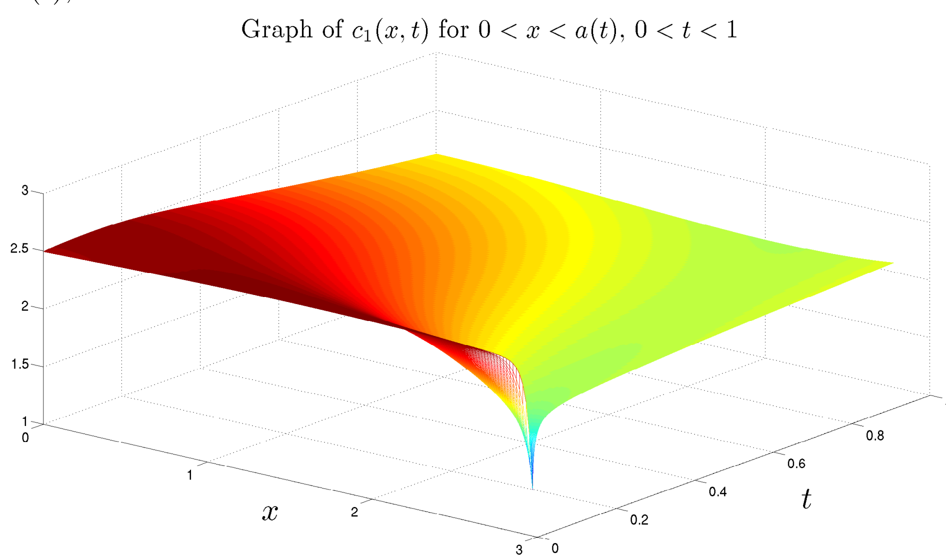

Figure 3.5: Graph of c_1 for $0 < x < a(t)$, $0 < t < 1$

We track the values ϕ, c_1 at $x = 0$ and ψ at $x = 5$, they all satisfy exponential decay to the equilibrium state, as shown below:

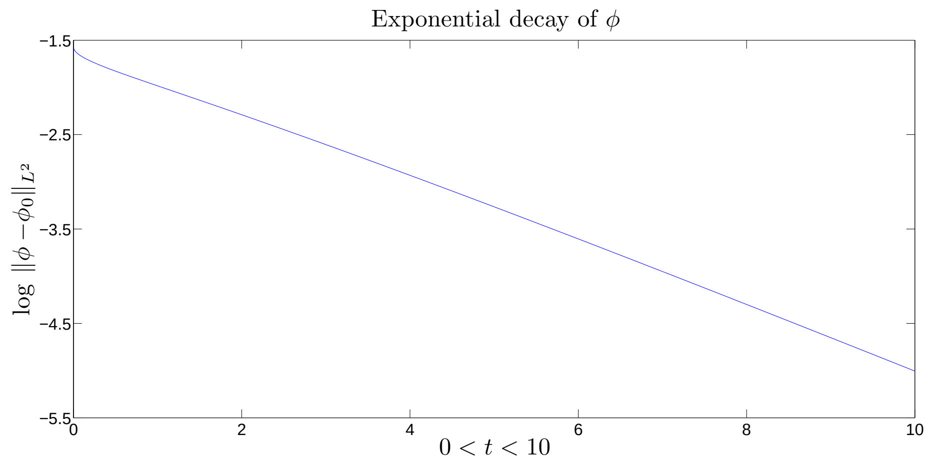

Figure 3.6: Exponential decay of $\|\phi\|_{L^2}$

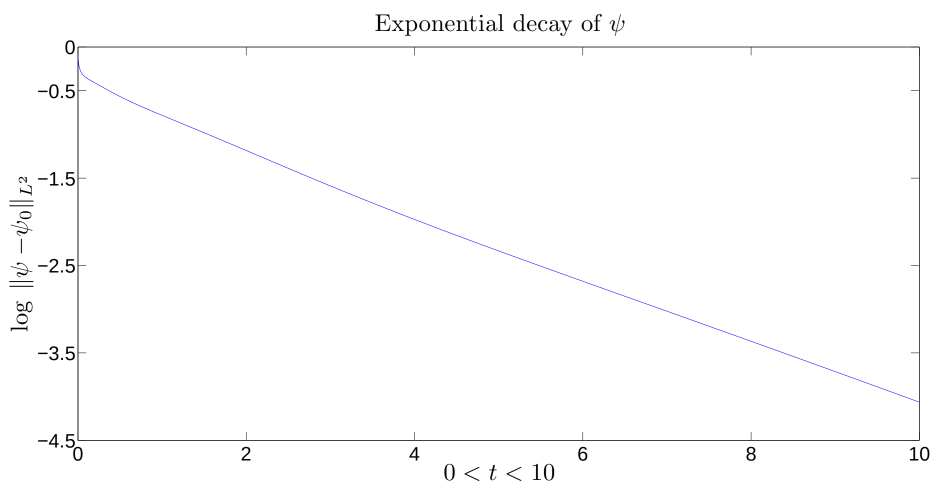

Figure 3.7: Exponential decay of $\|\psi\|_{L^2}$

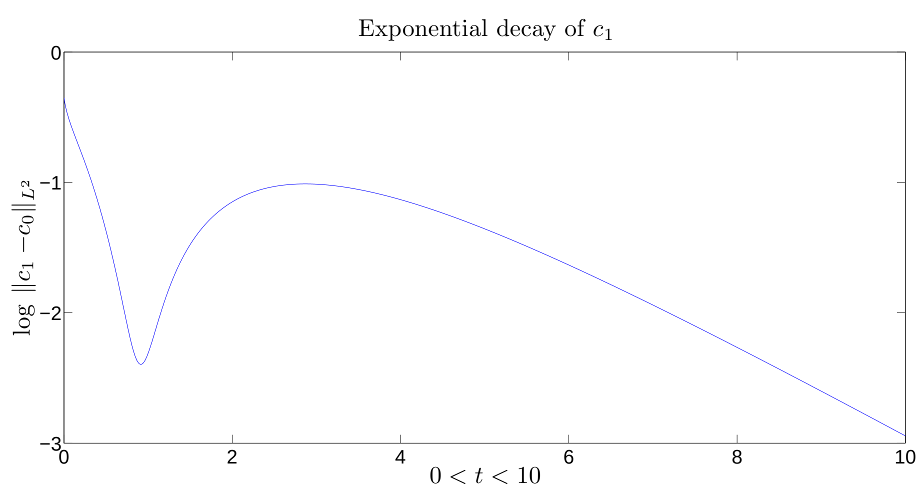

Figure 3.8: Exponential decay of $\|c_1\|_{L^2}$

and the linear approximation shows the rates are

$$\lambda_\phi \approx 0.349,\ \lambda_\psi \approx 0.349,\ \lambda_c \approx 0.344 \tag{3.300}$$

which match well with the theoretical value $\lambda \approx 0.349$ derived from (3.269).

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Appendix I: Onsager's principle for positive dielectric constant

We consider the system with ionic species, when the dielectric constant being nonzero. The electrostatic potential ψ no longer satisfies the electroneutral condition (3.46); instead, it satisfies Poisson equation (3.5). Except this, all the kinematic relations and constraints, boundary conditions are the same as mentioned in the first two paragraphs of section 3.3.

Define the potential energy $\mathcal{U}$ by

$$\begin{aligned}\mathcal{U} &= U + E_{\text{ion}} + E_{\text{elec}} \\ &= U + \int_{\Omega_t} \phi_2 \mathcal{W}_{\text{ion}}(c_k) + \mathcal{W}_{\text{elec}} d\mathbf{x} + \int_{\mathcal{R}_t} \mathcal{W}_{\text{ion}}(c_k) + \mathcal{W}_{\text{elec}} d\mathbf{x},\end{aligned} \tag{A-1}$$

in which (2.59), (3.1), (3.15) are satisfied. Define the Rayleigh dissipation function by

$$\begin{aligned}\mathcal{W} =& W + \sum_{k=1}^{N} \int_{\Omega_t} \frac{1}{2} k_B T D_k^{-1} \phi_2^2 c_k |\mathbf{u}_k - \mathbf{v}_2|^2 d\mathbf{x} \\ &+ \sum_{k=1}^{N} \int_{\mathcal{R}_t} \frac{1}{2} k_B T D_k^{-1} c_k |\mathbf{u}_k - \mathbf{v}_{\text{f}}|^2 d\mathbf{x},\end{aligned} \tag{A-2}$$

which is similar to (3.126). The stress tensors and body forces are defined by (2.34), (2.39), (2.41), (2.42), (3.6), (3.8). We state the Onsager's variational principle for $\epsilon \neq 0$ as follows.

Theorem A.1. *Let ϕ_i, $\mathbf{v}_{i,f}$, c_k, $\mathbf{u}_k$, ψ be smooth functions, ϕ_i, c_k, ψ satisfy* (3.5). *Let $\mathcal{U}$ be defined by* (A-1), *and $\dot{\mathcal{U}}$ be defined through the kinematic relations* (2.2), (2.30)-(2.33), (3.121)-(3.122) *and* (3.5)*(taking time derivative). Let*

$$Z \subset (C^2(\Omega_t))^{N+2} \times (C^2(\mathcal{R}_t))^{N+1} \tag{A-3}$$

be a subspace consisting of all elements $\{\mathbf{u}_1, \cdots, \mathbf{u}_N, \mathbf{v}_{1,2,f}\}$ *that* (2.3), (2.9), (2.11)-(2.13), (2.18), (3.123)-(3.124) *are satisfied. Suppose, for some* $\{\mathbf{u}_1, \cdots, \mathbf{u}_N, \mathbf{v}_{1,2,f}\} \in Z$, (2.4), (2.8) *with* $\gamma_{1,2} = 0$, (2.34), (2.41), (2.42), (2.39), (3.6), (3.8) *and boundary condition* (2.16), (2.44), (2.45), (3.10)-(3.13) *are all well defined and satisfied, then this element* $\{\mathbf{u}_1, \cdots, \mathbf{u}_N, \mathbf{v}_{1,2,f}\}$ *minimizes*

$$R = \dot{\mathcal{U}} + \mathcal{W} \tag{A-4}$$

in Z.

Proof. The main steps are similar to the proof of Theorem 2.3. We only present calculations that differs from the previous one. First, in order to calculate $\dot{\mathcal{U}}$ in Ω_t, we consider the electrostatic energy. Multiply (3.121) by $qz_k\psi$, integrate over Ω_t, and take sum from $k = 1$ to N,

$$\begin{aligned}
0 &= \int_{\Omega_t} \sum_{k=1}^{N} \left(qz_k\psi \frac{\partial(\phi_2 c_k)}{\partial t} + qz_k\psi\nabla\cdot(\phi_2 c_k \mathbf{u}_k) \right) d\mathbf{x} \\
&= \sum_{k=1}^{N} \frac{d}{dt}\int_{\Omega_t} qz_k\psi\phi_2 c_k d\mathbf{x} - \sum_{k=1}^{N}\int_{\Omega_t} \left(qz_k \frac{\partial \psi}{\partial t}\phi_2 c_k + \nabla\cdot(qz_k\psi\phi_2 c_k \mathbf{v}_1) \right) d\mathbf{x} \\
&+ \sum_{k=1}^{N}\int_{\Omega_t} qz_k\psi\nabla\cdot(\phi_2 c_k\mathbf{u}_k) d\mathbf{x} \\
&= \frac{d}{dt}\int_{\Omega_t}\sum_{k=1}^{N}(\phi_2 qz_k c_k)\,\psi d\mathbf{x} - \int_{\Omega_t}\sum_{k=1}^{N}(\phi_2 qz_k c_k)\frac{\partial\psi}{\partial t} d\mathbf{x} \\
&- \int_{\Omega_t}\sum_{k=1}^{N}(\phi_2 qz_k c_k\nabla\psi\cdot\mathbf{u}_k)d\mathbf{x} + \int_{\Gamma_t}\sum_{k=1}^{N} qz_k\psi\phi_2 c_k(\mathbf{u}_k - \mathbf{v}_1)\cdot\mathbf{n}dS \\
&=: S_1 - S_2 - \int_{\Omega_t}\sum_{k=1}^{N} qz_k\phi_2 c_k\nabla\psi\cdot\mathbf{u}_k d\mathbf{x} + \int_{\Gamma_t}\sum_{k=1}^{N} qz_k\psi\phi_2 c_k(\mathbf{u}_k - \mathbf{v}_1)\cdot\mathbf{n}dS
\end{aligned}$$

Integrating (3.5) by parts, we derive the following identities to replace S_1 and S_2 in the above:

$$
\begin{aligned}
S_1 &= \frac{d}{dt}\int_{\Omega_t} \left(-\nabla\cdot(\epsilon\nabla\psi) - \phi_1\rho_p\right)\psi d\mathbf{x} \\
&= \frac{d}{dt}\int_{\Omega_t} \epsilon|\nabla\psi|^2 d\mathbf{x} - \frac{d}{dt}\int_{\Gamma_t} \epsilon\psi\frac{\partial\psi}{\partial\mathbf{n}}dS - \frac{d}{dt}\int_{\Omega_t}\psi\phi_1\rho_p d\mathbf{x}; \\
S_2 &= \int_{\Omega_t}\frac{\partial\psi}{\partial t}\left(-\nabla\cdot(\epsilon\nabla\psi) - \phi_1\rho_p\right)d\mathbf{x} \\
&= \int_{\Omega_t}\epsilon\nabla\psi\nabla\frac{\partial\psi}{\partial t}d\mathbf{x} - \int_{\Gamma_t}\epsilon\frac{\partial\psi}{\partial t}\frac{\partial\psi}{\partial\mathbf{n}}dS - \int_{\Omega_t}\frac{\partial\psi}{\partial t}\phi_1\rho_p d\mathbf{x},
\end{aligned}
$$

recall (3.130), and it follows that

$$
\begin{aligned}
&\frac{d}{dt}\int_{\Omega_t}\phi_2\mathcal{W}_{\text{ion}} + \epsilon|\nabla\psi|^2 d\mathbf{x} \\
=&\int_{\Omega_t}\sum_{k=1}^{N}\left(\phi_2 c_k\nabla\left(\frac{\partial\mathcal{W}_{\text{ion}}}{\partial c_k}\right)\cdot(\mathbf{u}_k - \mathbf{v}_2) + qz_k\phi_2 c_k\nabla\psi\cdot\mathbf{u}_k\right) + \epsilon\nabla\psi\nabla\frac{\partial\psi}{\partial t}d\mathbf{x} \\
&+\frac{d}{dt}\int_{\Gamma_t}\epsilon\psi\frac{\partial\psi}{\partial\mathbf{n}}dS + \underline{\frac{d}{dt}\int_{\Omega_t}\psi\phi_1\rho_p d\mathbf{x} - \int_{\Omega_t}\frac{\partial\psi}{\partial t}\phi_1\rho_p d\mathbf{x}} + \int_{\Gamma_t} -\epsilon\frac{\partial\psi}{\partial t}\frac{\partial\psi}{\partial\mathbf{n}} \qquad \text{(A-5)} \\
&+\mathcal{W}_{\text{ion}}\phi_2(\mathbf{v}_1 - \mathbf{v}_2)\cdot\mathbf{n} \\
&+\sum_{k=1}^{N}\left(\frac{\partial\mathcal{W}_{\text{ion}}}{\partial c_k}\phi_2 c_k(\mathbf{v}_2 - \mathbf{u}_k)\cdot\mathbf{n} - qz_k\psi\phi_2 c_k(\mathbf{u}_k - \mathbf{v}_1)\cdot\mathbf{n}\right)dS.
\end{aligned}
$$

The underlined integrals can be simplified by

$$
\frac{d}{dt}\int_{\Omega_t}\psi\phi_1\rho_p d\mathbf{x} - \int_{\Omega_t}\frac{\partial\psi}{\partial t}\phi_1\rho_p d\mathbf{x} = \int_{\Omega_t}\phi_1\rho_p\nabla\psi\cdot\mathbf{v}_1 d\mathbf{x} = -\int_{\Omega_t} f_1^{\text{elec}}\cdot\mathbf{v}_1 d\mathbf{x},
$$

using (2.2)($i = 1$) and (3.6). Finally, we subtract the following identity from (A-5),

$$
\begin{aligned}
\frac{d}{dt}\int_{\Omega_t}\frac{1}{2}\epsilon|\nabla\psi|^2 d\mathbf{x} &= \int_{\Omega_t}\frac{1}{2}\frac{\partial\epsilon}{\partial t}|\nabla\psi|^2 + \epsilon\nabla\psi\cdot\nabla\frac{\partial\psi}{\partial t} + \int_{\Gamma_t}\frac{1}{2}\epsilon|\nabla\psi|^2(\mathbf{v}_1\cdot\mathbf{n})dS \\
&= \int_{\Omega_t}\frac{1}{2}\nabla\left(\frac{\partial\epsilon}{\partial\phi_1}|\nabla\psi|^2\right)\cdot(\phi_1\mathbf{v}_1) + \epsilon\nabla\psi\cdot\nabla\frac{\partial\psi}{\partial t}d\mathbf{x} \\
&+ \int_{\Gamma_t} -\frac{1}{2}\frac{\partial\epsilon}{\partial\phi_1}|\nabla\psi|^2(\phi_1\mathbf{v}_1)\cdot\mathbf{n} + \frac{1}{2}\epsilon|\nabla\psi|^2(\mathbf{v}_1\cdot\mathbf{n})dS,
\end{aligned}
$$

to get

$$
\begin{aligned}
&\frac{d}{dt}\int_{\Omega_t} \phi_2 \mathcal{W}_{\text{ion}} + \mathcal{W}_{\text{elec}} d\mathbf{x} \\
=&\int_{\Omega_t} \sum_{k=1}^{N} \left(\phi_2 c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot (\mathbf{u}_k - \mathbf{v}_2) + q z_k \phi_2 c_k \nabla \psi \cdot \mathbf{u}_k \right) \\
&- p_{\Delta}^{\text{elas}} \cdot \mathbf{v}_1 - f_1^{\text{elec}} \cdot \mathbf{v}_1 d\mathbf{x} + \int_{\Gamma_t} \mathcal{W}_{\text{ion}} \phi_2 (\mathbf{v}_1 - \mathbf{v}_2) \cdot \mathbf{n} \\
&+ \sum_{k=1}^{N} \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \phi_2 c_k (\mathbf{v}_2 - \mathbf{u}_k) \cdot \mathbf{n} - q z_k \psi \phi_2 c_k (\mathbf{u}_k - \mathbf{v}_1) \cdot \mathbf{n} \right) \\
&+ \frac{1}{2} \frac{\partial \epsilon}{\partial \phi_1} |\nabla \psi|^2 (\phi_1 \mathbf{v}_1) \cdot \mathbf{n} - \epsilon \frac{\partial \psi}{\partial t} \frac{\partial \psi}{\partial \mathbf{n}} - \frac{1}{2} \epsilon |\nabla \psi|^2 (\mathbf{v}_1 \cdot \mathbf{n}) dS + \frac{d}{dt} \int_{\Gamma_t} \epsilon \psi \frac{\partial \psi}{\partial \mathbf{n}} dS
\end{aligned}
\tag{A-6}
$$

For $\mathcal{R}_t$, it is similar to derive

$$
\begin{aligned}
&\frac{d}{dt}\int_{\mathcal{R}_t} \mathcal{W}_{\text{ion}} + \mathcal{W}_{\text{elec}} d\mathbf{x} \\
=&\int_{\mathcal{R}_t} \sum_{k=1}^{N} \left(c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot \mathbf{u}_k + q z_k c_k \nabla \psi \cdot \mathbf{u}_k \right) - k_B T \nabla c_k \cdot \mathbf{v}_{\text{f}} d\mathbf{x} \\
&+ \int_{\Gamma_t} -\mathcal{W}_{\text{ion}} (\mathbf{v}_1 \cdot \mathbf{n}) + \sum_{k=1}^{N} \left(c_k \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} (\mathbf{u}_k \cdot \mathbf{n}) + q z_k \psi c_k (\mathbf{u}_k - \mathbf{v}_1) \cdot \mathbf{n} \right) \\
&+ \epsilon \frac{\partial \psi}{\partial t} \frac{\partial \psi}{\partial \mathbf{n}} + \frac{1}{2} \epsilon |\nabla \psi|^2 (\mathbf{v}_1 \cdot \mathbf{n}) dS - \frac{d}{dt} \int_{\Gamma_t} \epsilon \psi \frac{\partial \psi}{\partial \mathbf{n}} dS \\
&+ \int_{\partial \mathbb{U}} \sum_{k=1}^{N} \left(-c_k \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} - q z_k \psi c_k \right) (\mathbf{u}_k \cdot \mathbf{n}) - \epsilon \frac{\partial \psi}{\partial t} \frac{\partial \psi}{\partial \mathbf{n}} dS - \frac{d}{dt} \int_{\partial \mathbb{U}} \epsilon \psi \frac{\partial \psi}{\partial \mathbf{n}} dS.
\end{aligned}
\tag{A-7}
$$

The integrals on the last line vanish, due to (3.124) and (3.13). Adding (A-6) and (A-7), we have

$$
\begin{aligned}
&\frac{d}{dt}\int_{\Omega_t} \phi_2 \mathcal{W}_{\text{ion}} + \mathcal{W}_{\text{elec}} d\mathbf{x} + \frac{d}{dt}\int_{\mathcal{R}_t} \mathcal{W}_{\text{ion}} + \mathcal{W}_{\text{elec}} d\mathbf{x} \\
=&\int_{\Omega_t} \sum_{k=1}^{N} \left(\phi_2 c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot (\mathbf{u}_k - \mathbf{v}_2) + q z_k \phi_2 c_k \nabla \psi \cdot \mathbf{u}_k \right) - (p_{\Delta}^{\text{elas}} + f_1^{\text{elec}}) \cdot \mathbf{v}_1 d\mathbf{x} \\
&+ \int_{\mathcal{R}_t} \sum_{k=1}^{N} \left(c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot \mathbf{u}_k + q z_k c_k \nabla \psi \cdot \mathbf{u}_k - k_B T \nabla c_k \cdot \mathbf{v}_{\text{f}} \right) d\mathbf{x}
\end{aligned}
$$

$$+\int_{\Gamma_t} \mathcal{W}_{\text{ion}}(-\phi_1\mathbf{v}_1 - \phi_2\mathbf{v}_2)\cdot\mathbf{n} + \sum_{k=1}^{N}(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k}\phi_2 c_k(\mathbf{v}_2 - \mathbf{u}_k^+)\cdot\mathbf{n}$$

$$+ c_k\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k}(\mathbf{u}_k\cdot\mathbf{n})) + \sum_{k=1}^{N}\left(-qz_k\phi_2 c_k\psi(\mathbf{u}_k^+ - \mathbf{v}_1)\cdot\mathbf{n} + qz_k c_k\psi(\mathbf{u}_k^- - \mathbf{v}_1)\cdot\mathbf{n}\right)$$

$$+ \frac{1}{2}\frac{\partial\epsilon}{\partial\phi_1}|\nabla\psi|^2(\phi_1\mathbf{v}_1)\cdot\mathbf{n} - \left[\epsilon\frac{\partial\psi}{\partial t}\frac{\partial\psi}{\partial\mathbf{n}}\right] - \left[\frac{1}{2}\epsilon|\nabla\psi|^2(\mathbf{v}_1\cdot\mathbf{n})\right]dS + \frac{d}{dt}\int_{\Gamma_t}\left[\epsilon\psi\frac{\partial\psi}{\partial\mathbf{n}}\right]dS. \tag{A-8}$$

Now we collect (A-1)-(A-4) and (A-8), apply (2.64) and (2.65), to derive $\mathcal{R}$:

$$\mathcal{R} = \int_{\Omega_t} -\nabla\cdot(\mathcal{T}_1 + \mathcal{S}_g)\cdot\mathbf{v}_1 - (\nabla\cdot\mathcal{T}_2)\cdot\mathbf{v}_2 + \frac{1}{2}\kappa|\mathbf{v}_1 - \mathbf{v}_2|^2$$

$$+ \sum_{k=1}^{N}\frac{1}{2}k_B T D_k^{-1}\phi_2^2 c_k|\mathbf{u}_k - \mathbf{v}_2|^2 + (\phi_1\mathbf{v}_1 + \phi_2\mathbf{v}_2)\cdot\nabla p d\mathbf{x}$$

$$+ \int_{\mathcal{R}_t} -(\nabla\cdot\mathcal{T}_f)\cdot\mathbf{v}_{\text{f}} + \sum_{k=1}^{N}\frac{1}{2}k_B T D_k^{-1}c_k|\mathbf{u}_k - \mathbf{v}_{\text{f}}|^2 + \mathbf{v}_{\text{f}}\cdot\nabla p d\mathbf{x}$$

$$+ A \text{ in } (2.65) + \text{ RHS of (A-8)}.$$

Due to incompressibility, the last integrand term in $\mathcal{R}_t$ can be replaced by a surface integral term:

$$\int_{\mathcal{R}_t}\sum_{k=1}^{N} -k_B T\nabla c_k\cdot\mathbf{v}_{\text{f}} d\mathbf{x} = -\int_{\Gamma_t}\sum_{k=1}^{N} k_B T c_k(\mathbf{v}_{\text{f}}\cdot\mathbf{n})dS.$$

Now (2.4), (2.8) and (3.136) can be derived from taking partial derivatives. For the boundary terms, our goal is to reach (2.16), (2.44) and (2.45). Since $\left[\epsilon\psi\frac{\partial\psi}{\partial\mathbf{n}}\right] = 0$ from (3.11), the very last integral in (A-8) vanishes. The remaining surface integral terms of (A-8) are:

$$\mathcal{W}_{\text{ion}}(-\phi_1\mathbf{v}_1 - \phi_2\mathbf{v}_2)\cdot\mathbf{n} + \sum_{k=1}^{N} c_k\frac{\partial\mathcal{W}_{\text{ion}}}{\partial c_k}(\phi_2\mathbf{v}_2 - \phi_2\mathbf{u}_k^+ + \mathbf{u}_k^-)\cdot\mathbf{n}$$

$$- \sum_{k=1}^{N} k_B T c_k(\mathbf{v}_{\text{f}}\cdot\mathbf{n}) - qz_k\phi_2 c_k\psi(\mathbf{u}_k^+ - \mathbf{v}_1)\cdot\mathbf{n} + qz_k c_k\psi(\mathbf{u}_k^- - \mathbf{v}_1)\cdot\mathbf{n}$$

$$+ A \text{ in } (2.65) + \frac{1}{2}\frac{\partial\epsilon}{\partial\phi_1}|\nabla\psi|^2(\phi_1\mathbf{v}_1)\cdot\mathbf{n} - \left[\epsilon\frac{\partial\psi}{\partial t}\frac{\partial\psi}{\partial\mathbf{n}}\right] - \left[\frac{1}{2}\epsilon|\nabla\psi|^2(\mathbf{v}_1\cdot\mathbf{n})\right],$$

We use (2.12), (3.11), (3.123) and the continuity of $\mathcal{W}_{\text{ion}}$ to eliminate terms on the first and second lines. Finally, we refer to (3.29)-(3.31), to derive:

$$\frac{1}{2}\frac{\partial \epsilon}{\partial \phi_1}|\nabla \psi|^2(\phi_1 \mathbf{v}_1)\cdot \mathbf{n} - \left[\epsilon \frac{\partial \psi}{\partial t}\frac{\partial \psi}{\partial \mathbf{n}}\right] - \left[\frac{1}{2}\epsilon |\nabla \psi|^2 (\mathbf{v}_1 \cdot \mathbf{n})\right] = \left[(\mathcal{S}^{\text{elec}}\mathbf{n})\cdot \mathbf{v}_1\right].$$

Consequently, all the boundary integral terms reduce to

$$A + \left[(\mathcal{S}^{\text{elec}}\mathbf{n})\cdot \mathbf{v}_1\right]. \tag{A-9}$$

Now, similar to the proof of theorem 2.2, it is easy to obtain the boundary conditions (2.16), (2.44) and (2.45). The proof is finished. □

Appendix II: Numerical scheme

We turn to the simulation part of our model. With or without ion species, the equations are defined on moving domains, and we discretize them at the reference configuration, let $0 < X < a_0$ be the gel region and $a_0 < X < L$ be the fluid region. We employ uniform grids in $(0, a_0)$ and in (a_0, L) with grid spacing h and h', respectively, and time step length Δt. Let M, M' and N_t be the total numbers of gel grids, fluid grids and time steps. For a function $u(t, X)$ define in $(0, a_0)$

$$u_m^n = u(n\Delta t, mh), \qquad D_{\alpha h}^0 u_m^n = \frac{u_{m+\alpha}^n - u_{m-\alpha}^n}{2\alpha h}, \tag{A-1}$$

$$D_h^+ u_m^n = \frac{u_{m+1}^n - u_m^n}{h}, \qquad D_h^- u_m^n = \frac{u_m^n - u_{m-1}^n}{h}, \tag{A-2}$$

and similar in (a_0, L) with $u_{m'}^n$, $D_{h'}^{0,\pm}$.

When there is no ion species in the system, the outside fluid region is trivial, and (2.67)-(2.79) is simplified to (2.82)-(2.83). At the reference configuration,

$$\left(\eta_1 \cdot \frac{v_X}{\varphi_X}\right)_X + \frac{\phi}{1-\phi}\left(\frac{\eta_2}{\varphi_X} \cdot \left(\frac{\phi v}{1-\phi}\right)_X\right)_X + \left(f(\phi) - \phi f'(\phi)\right)_X = \frac{\kappa v \varphi_X}{(1-\phi)^2}, \tag{A-3}$$

$$-\eta_\perp v = \eta_1 \cdot \frac{v_X}{\varphi_X} + \frac{\phi}{1-\phi}\frac{\eta_2}{\varphi_X} \cdot \left(\frac{\phi v}{1-\phi}\right)_X + f(\phi) - \phi f'(\phi) \quad \text{at} \quad X = a_0 \tag{A-4}$$

in which $\varphi = \varphi(t, X)$, $X \in (0, a_0)$ is the deformation map, and $v = v_1 = \varphi_t$, $\phi = \phi_1 = \phi_0(\varphi_X)^{-1}$. We discretize (A-3) at $X = mh$, $m = 1, \cdots, M-1$:

$$\begin{aligned} &\eta_1 D_h^- \left(\frac{D_h^+ v_m}{D_h^+ \varphi_m^n}\right) + \eta_2 \frac{\phi_m^n}{1-\phi_m^n} \cdot D_h^- \left((D_h^+ \varphi_m^n)^{-1} \cdot D_h^+ \left(\frac{\phi_m^n v_m}{1-\phi_m^n}\right)\right) \\ &+ D_h^- \left(f(\phi_{m+0.5}^n) - \phi_{m+0.5}^n f'(\phi_{m+0.5}^n)\right) = \frac{\kappa v_m}{(1-\phi_m^n)^2} \cdot D_h^0 \varphi_m^n \end{aligned} \tag{A-5}$$

and (A-4) at $X = Mh = a_0$:

$$\begin{aligned}-\eta_\perp v_M =& \eta_1 D_h^- \left(\frac{D_h^- v_M}{D_h^- \varphi_M^n}\right) + \eta_2 \frac{\phi_M^n}{1-\phi_M^n} \cdot (D_h^- \varphi_M^n)^{-1} \cdot D_h^- \left(\frac{\phi_M^n v_M}{1-\phi_M^n}\right) \\ &+ f(\phi_{M-0.5}^n) - f'(\phi_{M-0.5}^n)\end{aligned} \tag{A-6}$$

in which

$$v_m = \frac{\varphi_m^{n+1} - \varphi_m^n}{\Delta t}, \quad \phi_{m-0.5}^n = \frac{(\phi_0)_{m-0.5}}{D_{0.5h}^0 \varphi_{m-0.5}^n}, \quad \phi_m = \frac{1}{2}(\phi_{m-0.5} + \phi_{m+0.5}), \tag{A-7}$$

some terms at $X = Mh$ are approximated by those at $X = (M-2)h$ and $X = (M-1)h$. It is possible to maintain the energy dissipation identity

$$\begin{aligned}\frac{d}{dt}\int_0^a f(\phi)dx =& -\int_0^a \left(\sum_{i=1}^2 \eta_i |v_{i,x}|^2 + \kappa |v_1 - v_2|^2\right) dx - \eta_\perp \omega^2\Big|_{x=a} \\ =& -\int_0^a \left(\eta_1 |v_x|^2 + \eta_2 \left|\left(\frac{\phi v}{1-\phi}\right)_x\right|^2 + \frac{\kappa v^2}{(1-\phi)^2}\right) dx - \eta_\perp v^2\Big|_{x=a}\end{aligned} \tag{A-8}$$

after the discretization, if we express the energy derivative by

$$f'(\phi_m^n) = \begin{cases} \frac{f(\phi_m^{n+1}) - f(\phi_m^n)}{\phi_m^{n+1} - \phi_m^n} & \text{if} \quad \phi_m^{n+1} \neq \phi_m^n; \\ f'(\phi), \quad \phi = \phi_m^n & \text{if} \quad \phi_m^{n+1} = \phi_m^n. \end{cases} \tag{A-9}$$

In fact, multiply (A-5) by v_m and integrate by parts, using (A-6), the only pivotal part is to maintain

$$\frac{d}{dt}\int_0^{a_0} f(\phi)\varphi_X dX = \int_0^{a_0} v\left(f(\phi) - \phi f'(\phi)\right)_X dX \tag{A-10}$$

at the discrete level. If $\phi_m^{n+1} = \phi_m^n$, there is no problem for this m. For convenience, we assume equality does not occur, then

$$\begin{aligned}&\sum_{m=1}^{M-1} v_m \cdot D_h^- \left(f(\phi_{m+0.5}^n) - \phi_{m+0.5}^n f'(\phi_{m+0.5}^n)\right) \\ &- \frac{v_M}{h}\left(f(\phi_{M-0.5}^n) - \phi_{M-0.5}^n f'(\phi_{M-0.5}^n)\right)\end{aligned}$$

$$
\begin{aligned}
&= -\sum_{m=0}^{M-1} D_h^+ v_m \cdot \left(f(\phi_{m+0.5}^n) - \phi_{m+0.5}^n f'(\phi_{m+0.5}^n) \right) \\
&= -\sum_{m=0}^{M-1} D_h^+ v_m \cdot f(\phi_{m+0.5}^n) + \sum_{m=0}^{M-1} \frac{1}{\Delta t} \left(\frac{D_h^+ \varphi_m^{n+1}}{D_h^+ \varphi_m^n} - 1 \right) (\phi_0)_{m+0.5} f'(\phi_{m+0.5}^n) \\
&= -\sum_{m=0}^{M-1} D_h^+ v_m \cdot f(\phi_{m+0.5}^n) \\
&\quad + \frac{1}{\Delta t} \sum_{m=0}^{M-1} D_h^+ \varphi_m^{n+1} \cdot \left(\frac{1}{D_h^+ \varphi_m^n} - \frac{1}{D_h^+ \varphi_m^{n+1}} \right) (\phi_0)_{m+0.5} f'(\phi_{m+0.5}^n) \\
&= -\frac{1}{\Delta t} \sum_{m=0}^{M-1} (D_h^+ \varphi_{m+1}^{n+1} - D_h^+ \varphi_{m+1}^n) f(\phi_{m+0.5}^n) \\
&\quad - \frac{1}{\Delta t} \sum_{m=0}^{M-1} D_h^+ \varphi_m^{n+1} \cdot \left(f(\phi_{m+0.5}^{n+1}) - f(\phi_{m+0.5}^n) \right) \\
&= -\frac{1}{\Delta t} \sum_{m=0}^{M-1} \left(D_h^+ \varphi_m^{n+1} f(\phi_{m+0.5}^{n+1}) - D_h^+ \varphi_m^n f(\phi_{m+0.5}^n) \right), \qquad \text{(A-11)}
\end{aligned}
$$

the boundary terms on the first line cancel with the ones in (A-6), and the energy dissipation is guaranteed.

Now consider the model with ion species. We have simplified the equations as (3.163)-(3.174). At the reference configuration, introduce new variables

$$
u_k = \begin{cases} c_k \cdot (\varphi_X - \phi_0) & \text{when } 0 < X < a_0; \\ c_k \cdot \frac{L-a}{L-a_0} & \text{when } a_0 < X < L. \end{cases} \qquad \text{(A-12)}
$$

for k-th ion. The constitutive equations for u_k can be written in divergence form, hence we apply the finite volume method for u_k. In $(0, a_0)$, the diffusion equations and neutrality equations

$$
(u_k)_t = \left(\frac{v u_k}{\varphi_X - \phi_0} \right)_X + \left(\frac{D_k}{\varphi_X} \left(\frac{u_k}{\varphi_X - \phi_0} \right)_X + \frac{D_k z_k \psi_X}{\varphi_X} \cdot \frac{u_k}{\varphi_X - \phi_0} \right)_X, \qquad \text{(A-13)}
$$

$$
\sum_{k=1}^{N} z_k u_k + \phi_0 \rho_p = 0, \qquad \text{(A-14)}
$$

are discretized at $0.5h, \cdots, (M-1.5)h$ in the following manner:

$$\frac{(u_k)^{n+1}_{m-0.5} - (u_k)^n_{m-0.5}}{\Delta t} = (j_k)^{n+1}_m - (j_k)^{n+1}_{m-1}, \quad h \cdot (j_k)^{n+1}_m =$$

$$\frac{v_m (u_k)^{n+1}_m}{D^+_h \varphi^n_m - (\phi_0)_m} + \frac{(D_k)_m}{D^+_h \varphi^n_m} D^0_{0.5h} \left(\frac{(u_k)^{n+1}_m}{D^0_{0.5h}\varphi^n_m - (\phi_0)_m} \right) + \frac{(D_k)_m z_k (u_k)^{n+1}_m D^0_{0.5h} \psi^{n+1}_m}{D^+_h \varphi^n_m \left(D^+_h \varphi^n_m - (\phi_0)_m \right)}, \tag{A-15}$$

$$\sum_{k=1}^{N} z_k (u_k)^{n+1}_{m-0.5} + (\phi_0)_{m-0.5} \rho_p = 0. \tag{A-16}$$

Here, $(j_k)_m$ is the flux at $X = mh$, $m = 1, \cdots, M-1$, $(j_k)_0 = 0$, D_k may be non-constant, $(u_k)^{n+1}_m$ is the average of $(u_k)^{n+1}_{m-0.5}$ and $(u_k)^{n+1}_{m+0.5}$, the neutrality equation at $(M-0.5)h$ is also required. We use the implicit scheme to solve for u^{n+1} and ψ^{n+1}, which has two advantages: first, the neutrality constraint must be satisfied at $t = (n+1)\Delta t$, it is very difficult to find an explicit scheme which has such property, if the dielectric constant becomes positive hence the neutrality constraint becomes Poisson equation, the explicit scheme cannot work out; second, the implicit scheme is less restrictive on the size of Δt compared to the explicit scheme, which is very beneficial when we choose small h. Also, notice that we do not use the fully backward scheme: while applying Newton's method to solve the nonlinear equations, it is technically more convenient to use φ^n in the diffusion equations.

The rightmost grid in the gel region is combined with the leftmost grid in the fluid region, this may avoid the interface flux condition. We have:

$$\frac{(u_k)^{n+1}_{M-0.5} - (u_k)^n_{M-0.5}}{\Delta t} + \frac{(u_k)^{n+1}_{0.5'} - (u_k)^n_{0.5'}}{\Delta t} = (j_k)^{n+1}_{1'} - (j_k)^{n+1}_{m-1}, \quad h' \cdot (j_k)^{n+1}_{m'} =$$

$$\frac{L - X_{m'}}{L - a_0} v_M (u_k)^{n+1}_{m'} + (D_k)_{m'} \left(\frac{L-a_0}{L-a} \right)^2 \left(D^0_{0.5h'} (u_k)^{n+1}_{m'} + (u_k)^{n+1}_{m'} z_k D^0_{0.5h'} \psi^{n+1}_{m'} \right),$$

$$\text{in which } \; X_{m'} = a_0 + mh', \;\; a = \varphi^n_M, \;\; (u_k)^{n+1}_{m'} = \frac{1}{2}\left((u_k)^{n+1}_{(m-0.5)'} + (u_k)^{n+1}_{(m+0.5)'} \right). \tag{A-17}$$

The diffusion equations and neutrality equations are similar in (a_0, L):

$$(u_k)_t = v(a_0) \cdot \left(u_k \cdot \frac{L-X}{L-a} \right)_X + \left(\frac{L-a_0}{L-a} \right)^2 \left(D_k (u_k)_X + D_k u_k z_k \psi_X \right)_X, \tag{A-18}$$

$$\sum_{k=1}^{N} z_k u_k = 0. \tag{A-19}$$

Accordingly, at $a_0 + 1.5h', \cdots, a_0 + (M-0.5)h'$, we have

$$\frac{(u_k)^{n+1}_{(m-0.5)'} - (u_k)^{n}_{(m-0.5)'}}{\Delta t} = (j_k)^{n+1}_{m'} - (j_k)^{n+1}_{(m-1)'}, \tag{A-20}$$

$$\sum_{k=1}^{N} z_k (u_k)^{n+1}_{(m-0.5)'} = 0. \tag{A-21}$$

Here, $(j_k)_{m'}$ is defined in (A-17), $(j_k)^{n+1}_{M'} = 0$, and the neutrality equation at $a_0+0.5h'$ is also required. For interface conditions, we use $(u_k)^{n+1}_{m-0.5}$, $(u_k)^{n+1}_{0.5'}$ and $\psi^{n+1}_{m-0.5}$, $\psi^{n+1}_{0.5'}$ to represent the corresponding values at $X = a_0$. The discretizations are the same as above, we only list the equations at the reference configuration:

$$\ln\left(\frac{u_k^+}{\varphi_X - \phi_0}\right) - \ln\left(u_k^- \cdot \frac{L-a_0}{L-a}\right) + z_k\left[\psi\right] = 0, \tag{A-22}$$

$$\begin{aligned} -\eta_\perp v =& \frac{\eta_1 v_X}{\varphi_X} + \frac{\phi}{1-\phi}\frac{\eta_2}{\varphi_X}\left(\frac{\phi v}{1-\phi}\right)_X + f(\phi) - \phi f'(\phi) \\ &- \sum_{k=1}^{N}\left(\frac{u_k^+}{\varphi_X - \phi_0} - u_k^- \cdot \frac{L-a_0}{L-a}\right). \end{aligned} \tag{A-23}$$

Finally, we have the ionic version of the momentum equation for which

$$-\frac{\phi\rho_p}{1-\phi}\psi_X \approx -\frac{\phi^n_m \rho_p}{1-\phi^n_m} D^0_{0.5h}\psi^{n+1}_m$$

is added to the left hand side of (A-5). The energy dissipation identity with ion species is difficult to maintain, mainly because the diffusion equations and the momentum equation are discretized at different locations, and the interface conditions are difficult to handle. We do not expect this property in the ionic situation.