

ANALYSIS AND SIMULATION OF A MODEL OF POLYELECTROLYTE GEL IN ONE SPATIAL DIMENSION

HAORAN CHEN, MARIA-CARME CALDERER, YOICHIRO MORI

Abstract. We analyze a model of polyelectrolyte gels that was proposed by the authors in previous work. We first demonstrate that the model can be derived using Onsager’s variational principle, a general procedure for obtaining equations in soft condensed matter physics. The model is shown to have a unique steady state under the assumption that a suitably defined mechanical energy density satisfies a convexity condition. We then perform a detailed study of the stability of the steady state in the spatially one-dimensional case, obtaining bounds on the relaxation rate. Numerical simulations for the spatially one-dimensional problem are presented, confirming the analytical calculations on stability.

1. Introduction. Gels are crosslinked, three dimensional polymer networks that absorb solvent and swell without dissolution [21, 22, 16, 39, 2]. In this paper, we study polyelectrolyte gels, in which the polymer network carries charge, and delivers counterions to the solvent. An important feature of many polyelectrolyte gels is that they undergo large and often discontinuous volume changes (called the volume phase transition) in response to various environmental parameters, including pH, temperature and ionic composition [14, 37, 38]. Some physically interesting characteristics of the volume phase transition include robust hysteresis, coexistence of phases and complicated transient dynamics [12, 37]. These volume changes are at the basis of numerous applications of gels to artificial devices [3, 31, 29, 7, 13, 19] and are thought to underlie certain physiological processes [46, 41, 37, 29]. It is thus of both practical and theoretical interest to develop a dynamic model of polyelectrolyte gels.

There have been numerous modeling studies of gels. Studies using purely mechanical models include [36, 40] in which static problems are addressed, and [5, 44, 35, 9, 10, 24, 25] in which dynamic problems are the focus. Models of polyelectrolyte gels include the static models of [37, 20, 34] and the dynamic models of [17, 15, 18, 26, 28, 43, 42, 45, 27, 6, 1, 20]. In this paper, we initiate a detailed study of a dynamic PDE model of polyelectrolyte gels introduced in [30]. Our model is distinguished from previous models in its careful derivation of the boundary conditions at the gel-fluid interface as well as its satisfaction of a free energy identity, including interfacial terms. We show that our model can be derived from Onsager’s variational principle which is a systematic way of deriving equations in soft condensed matter systems [10, 33]. The one-dimensional stability calculation is a generalization of the classical work by [40] in which the neutral gel case is studied. We prove the uniqueness of the steady state solution and study the stability as the model being restricted to one spatial dimension. Finally, we have successfully simulated our polyelectrolyte gel model in the one spatial dimension. The simulated equilibrium solution and exponential decay rate both match our analytical calculation.

The paper is organized as follows. In section 2, we apply Onsager’s variational principle to a purely mechanical model of gel dynamics. First, we illustrate the principle by analyzing a simple mechanical example. Then, we turn to our gel model and define the energy relation, clarify the kinematic relations and kinematic constraints, and show that the dynamic equations and boundary conditions follow from Onsager’s variational principle. In section 3, we treat the case of polyelectrolyte gel. In this model, the polymer network carries charge and soluble ions undergo electrodiffusion. We shall see that Onsager’s variational principle may be used to derive this model as well.

In section 4, we analyze 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. We clarify the dependence of the eigenvalues of the linearized equations on key parameters such as friction coefficient, permeability and viscosity. The sequence of eigenvalues in the purely mechanical model may be seen as decay rates intrinsic to the polymer phase, an interpretation that will later aid in gaining insight into the ionic case.

Section 5 is divided into three parts. First, we present and show uniqueness of the steady state solution, under certain assumptions on the form of the mechanical energy density. Secondly, we consider a simple situation when the outside solution is always well mixed. The smallest eigenvalue found in section 4, which we call 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. Lastly, we consider a case involving dynamics of the outside solution, and show that under certain assumptions, the minimal decay rate must exceed the slowest decay rates of gel and ion species considered in isolation.

Numerical simulations are presented in section 6, in which we show a typical example of a one-dimensional two-ion system. After a transient period of fast movement near the gel-fluid interface, the gel and ions quickly approach the steady state. The numerically computed exponential decay rate matches the computational result in section 5.

In the polyelectrolyte gel model, we assumed electroneutrality. Onsager's variational principle may also be applied to our model with positive dielectric constant. In that situation, the electroneutrality is replaced by the Poisson equation, and the Maxwell stress tensor and the Helmholtz force are introduced. We put the detailed computation in the appendix I.

2. Mechanical model and energy dissipation principle. Our goal in this section is to derive the equations for gel dynamics using Onsager's variational principle [10]. The gel dynamics equations of this paper were first presented in [30], and the derivation there relied on physical arguments. 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 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, \dots, m_N , their positions x_1, \dots, x_N and velocities v_1, \dots, v_N which satisfy

$$m_i \frac{dv_i}{dt} = -\gamma_i v_i - \sum_{j \neq i} \gamma_{ij} (v_i - v_j) - kx_i \quad \text{for } i = 1, \dots, N \quad (2.1)$$

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

$$\gamma_i v_i + \sum_{j \neq i} \gamma_{ij} (v_i - v_j) = -kx_i \quad \text{for } i = 1, \dots, N \quad (2.2)$$

We impose the condition that $\gamma_{ij} = \gamma_{ji}$, in this case, a simple consequence of Newton's third law. As we shall see, Onsager's variational principle can only be applied when this reciprocity is satisfied.

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

$$\frac{dx_i}{dt} = v_i. \quad (2.3)$$

Let us multiply both sides of (2.2) with v_i and take the summation in i . With the help of (2.3), we obtain the following *energy relation*:

$$\frac{dU}{dt} = -2W, \quad U = \sum_{i=1}^N \frac{1}{2} kx_i^2, \quad 2W = \sum_{i=1}^N \gamma_i v_i^2 + \frac{1}{2} \sum_{i \neq j} \gamma_{ij} (v_i - v_j)^2. \quad (2.4)$$

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 (2.3) and the energy relation (2.4). Consider the expression:

$$R = \frac{dU}{dt} + W = \sum_{i=1}^N \frac{\partial U}{\partial x_i} \frac{dx_i}{dt} + W(v_1, \dots, v_N) = \sum_{i=1}^N \frac{\partial U}{\partial x_i} v_i + W(v_1, \dots, v_N), \quad (2.5)$$

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

$$\frac{\partial R}{\partial v_i} = kx_i + \gamma_i v_i + \sum_{j \neq i} \frac{1}{2} (\gamma_{ij} + \gamma_{ji}) (v_i - v_j) = 0 \text{ for } i = 1, \dots, N. \quad (2.6)$$

Noting that $\gamma_{ij} = \gamma_{ji}$, we recover the dynamic equation (2.2). 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 [10]. There are several possible advantages of this variational approach [11]. 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.

We now turn to the main topic of this section. We derive the equations of gel dynamics using Onsager's variational principle. In [30], we stated the kinematic relations and proposed the dynamic equations, from which the energy relation was derived as a consequence. Here, we start from the kinematic and energy relations, and using the variational approach, to derive the dynamic equations. In this section, we consider the case without ions. The electro-diffusion of ions will be incorporated in the next section.

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 $\mathbb{U} \subset \mathbb{R}^3$ which is fixed. Let Ω be the reference domain of the polymer network, and $\Omega_t \subset \mathbb{U}$ for the network at time t . We assume that the gel is completely immersed in the fluid, $\Gamma_t \equiv \partial\Omega_t, \Gamma_t \cap \partial\mathbb{U} = \emptyset$, and denote the fluid region by $\mathcal{R}_t \equiv \mathbb{U} \setminus (\Omega_t \cup \Gamma_t)$. A point $\mathbf{X} \in \Omega$ is mapped to a point $\mathbf{x} \in \Omega_t$ by the smooth deformation map φ_t :

$$\mathbf{x} = \varphi_t(\mathbf{X}). \quad (2.7)$$

Let $\mathbf{v}_{i,f}$, $i = 1, 2$ be the velocities of the polymer and solvent components in Ω_t , and the velocity of fluid in \mathcal{R}_t respectively. Throughout the paper we use indexes $\{1, 2, f\}$ or $\{i, f\}$ to denote variables for polymer, solvent and surrounding fluid, respectively. Then v_1 and φ_t are related by

$$\mathbf{v}_1(\varphi_t(\mathbf{X}), t) = \frac{\partial}{\partial t}(\varphi_t(\mathbf{X})). \quad (2.8)$$

We let $F = \nabla_X \varphi_t$ be the deformation gradient, $\mathcal{F} = F \circ \varphi_t^{-1}$ be the deformation gradient evaluated in Ω_t . It follows that:

$$\left. \frac{\partial F}{\partial t} \right|_{\mathbf{x}=\varphi_t^{-1}(\mathbf{x})} = \frac{\partial \mathcal{F}}{\partial t} + (\mathbf{v}_1 \cdot \nabla) \mathcal{F} = (\nabla \mathbf{v}_1) \mathcal{F}. \quad (2.9)$$

The volume fractions ϕ_1 and ϕ_2 satisfy the *kinematic relations*:

$$(\phi_1 \circ \varphi_t) \det F = \phi_I; \quad (2.10)$$

$$\frac{\partial \phi_i}{\partial t} + \nabla \cdot (\mathbf{v}_i \phi_i) = 0, \quad i = 1, 2; \quad (2.11)$$

where ϕ_I is the initial data on Ω . Now we turn to the *kinematic constraints*. In \mathcal{R}_t , we have the incompressibility constraint

$$\nabla \cdot \mathbf{v}_f = 0. \quad (2.12)$$

In Ω_t , we require that the volume fractions add to 1:

$$\phi_1 + \phi_2 = 1. \quad (2.13)$$

This statement is equivalent to having $\phi_1 + \phi_2 = 1$ at $t = 0$ and requiring

$$\nabla \cdot (\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) = 0, \quad \forall t > 0, \quad x \in \Omega_t. \quad (2.14)$$

As we shall see, Onsager's variational principle works well with constraints that are linear in the velocities, and therefore, we will find (2.14) more convenient for our purposes than (2.13).

At the boundary, we impose the following conditions. 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 , we have

$$\mathbf{v}_1 \cdot \mathbf{n} = v_\Gamma \text{ on } \Gamma_t. \quad (2.15)$$

The conservation of mass gives:

$$(\mathbf{v}_f - \mathbf{v}_1) \cdot \mathbf{n} = \phi_2 (\mathbf{v}_2 - \mathbf{v}_1) \cdot \mathbf{n} := w, \quad (2.16)$$

and we assume that the tangential velocities of the fluid on both sides of the surface Γ are continuous:

$$(\mathbf{v}_f - \mathbf{v}_1)_\parallel = (\mathbf{v}_2 - \mathbf{v}_1)_\parallel := \mathbf{q}. \quad (2.17)$$

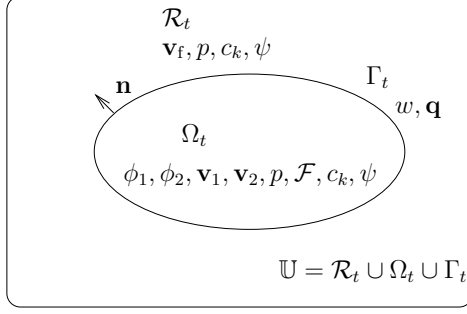


FIG. 2.1. Set up of the model

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

$$\mathbf{v}_f = 0. \quad (2.18)$$

This implies that we are not injecting energy into the system. This has important implications for the steady state and stability calculations in Section 4 and 5.

Now we introduce the energies. The total energy of the system is given as the sum of the elastic and Flory-Huggins energies

$$U = E_{\text{FH}} + E_{\text{elas}} = \int_{\Omega_t} \mathcal{W}_{\text{FH}}(\phi_1) + \phi_1 \mathcal{W}_{\text{elas}}(\mathcal{F}) d\mathbf{x}, \quad (2.19)$$

for which

$$\begin{aligned} \mathcal{W}_{\text{elas}} &= \mathcal{W}_{\text{elas}}(\mathcal{F}); \\ \mathcal{W}_{\text{FH}} &= \mathcal{W}_{\text{FH}}(\phi_1) = a\phi_1 \ln \phi_1 + b\phi_2 \ln \phi_2 + c\phi_1\phi_2. \end{aligned} \quad (2.20)$$

Throughout the paper we neglect inertial effects, so the kinetic energy is not considered.

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

$$\begin{aligned} W &= \int_{\Omega_t} \left(\frac{1}{2} \kappa |\mathbf{v}_1 - \mathbf{v}_2|^2 + \sum_{i=1}^2 \eta_i \|\nabla_S \mathbf{v}_i\|^2 \right) d\mathbf{x} + \int_{\mathcal{R}_t} \eta_f \|\nabla_S \mathbf{v}_f\|^2 d\mathbf{x} \\ &+ \int_{\Gamma_t} \frac{1}{2} (\eta_{\perp} w^2 + \eta_{\parallel} |\mathbf{q}|^2) dS, \end{aligned} \quad (2.21)$$

in which $\nabla_S \cdot = \frac{1}{2}(\nabla \cdot + \nabla^T \cdot)$ is the symmetric part of the corresponding velocity gradient. The quadratic term with κ corresponds to friction, and κ may depend on ϕ_1 ; the quadratic terms with $\eta_{i,f}$ correspond to viscosity, and $\eta_{i,f}$ are positive and may depend on ϕ_1 ; the boundary terms correspond to interface friction, in the normal and tangential directions.

Given the above kinematic relations, kinematic constraints and energy relations (total energy and Rayleigh's dissipation form), we are ready to apply Onsager's variational principle to derive all of dynamic equations and boundary conditions, which we list here for future reference. We note that a similar derivation of both the dynamic equations and boundary conditions for the contact line problem is performed in [33].

We propose force balances in the gel and in the outer fluid:

$$\nabla \cdot \mathcal{T}_i - \phi_i \nabla p + \mathbf{f}_i = 0, \quad i = 1, 2 \quad \text{in } \Omega_t, \quad (2.22)$$

$$\nabla \cdot \mathcal{T}_f - \nabla p + \mathbf{f}_f = 0, \quad \text{in } \mathcal{R}_t, \quad (2.23)$$

$$\mathcal{T}_1 = \mathcal{T}_1^{\text{visc}} + \mathcal{T}_1^{\text{elas}} + \mathcal{T}_1^{\text{FH}}, \quad \mathcal{T}_{2,f} = \mathcal{T}_{2,f}^{\text{visc}}, \quad (2.24)$$

in which p is mechanical pressure, $\mathcal{T}_{i,f}$ are stress tensors, including elastic, Flory-Huggins and viscous stresses

$$\begin{aligned} \mathcal{T}_1^{\text{elas}} &= \phi_1 \frac{\partial \mathcal{W}_{\text{elas}}(\mathcal{F})}{\partial \mathcal{F}} \mathcal{F}^T, \\ \mathcal{T}_1^{\text{FH}} &= \left(\mathcal{W}_{\text{FH}}(\phi_1) - \phi_1 \left(\frac{d}{d\phi_1} \mathcal{W}_{\text{FH}}(\phi_1) \right) \right) I \\ \mathcal{T}_{1,2,f}^{\text{visc}} &= \eta_{1,2,f} (\nabla \mathbf{v}_{1,2,f} + (\nabla \mathbf{v}_{1,2,f})^T), \end{aligned} \quad (2.25)$$

and $f_{i,f}$ are frictions (in the mechanical case)

$$\mathbf{f}_1 = \mathbf{f}^{\text{fric}} = -\kappa(\mathbf{v}_1 - \mathbf{v}_2), \mathbf{f}_2 = -\mathbf{f}^{\text{fric}}, \mathbf{f}_f = 0. \quad (2.26)$$

We propose balance of forces across the interface, in the normal and tangential directions:

$$\mathcal{T}_f \mathbf{n} - \mathcal{T}_1 \mathbf{n} - \mathcal{T}_2 \mathbf{n} + [p] \mathbf{n} = 0; \quad (2.27)$$

$$\eta_{\perp} w = \Pi_{\perp} = \mathbf{n} \cdot (\mathcal{T}_f \mathbf{n}) - \mathbf{n} \cdot \left(\frac{\mathcal{T}_2}{\phi_2} \right) \mathbf{n} + [p]; \quad (2.28)$$

$$\eta_{\parallel} \mathbf{q} = \Pi_{\parallel} \equiv (\mathcal{T}_1 \mathbf{n})_{\parallel}. \quad (2.29)$$

Here, $[p] := p^+ - p^-$ denotes the jump of pressure across Γ_t , and the indexes $\{\perp, \parallel\}$ stand for the normal component and the tangential component, respectively; η_{\perp} and η_{\parallel} are positive constants. Notice that η_{\perp} measures permeability of gel: when $\eta_{\perp} = 0$, the gel is fully permeable; as it increases, the gel becomes more impermeable.

Now we apply Onsager's principle to derive (2.22)-(2.29). Denote \dot{U} as

$$\begin{aligned} \dot{U} &= \frac{dU}{dt} \\ &= \int_{\Omega_t} \frac{d\mathcal{W}_{\text{FH}}}{d\phi_1} \frac{\partial \phi_1}{\partial t} + \nabla \cdot (\mathcal{W}_{\text{FH}} \mathbf{v}_1) d\mathbf{x} + \frac{d}{dt} \int_{\Omega} \phi_I \mathcal{W}_{\text{elas}}(F) d\mathbf{X} \\ &= \int_{\Omega_t} -\frac{d\mathcal{W}_{\text{FH}}}{d\phi_1} \nabla \cdot (\phi_1 \mathbf{v}_1) + \nabla \cdot (\mathcal{W}_{\text{FH}} \mathbf{v}_1) d\mathbf{x} + \int_{\Omega} \phi_I \frac{\partial \mathcal{W}_{\text{elas}}(F)}{\partial F} : \frac{\partial F}{\partial t} d\mathbf{X} \\ &= \int_{\Omega_t} -\frac{d\mathcal{W}_{\text{FH}}}{d\phi_1} \nabla \cdot (\phi_1 \mathbf{v}_1) + \nabla \cdot (\mathcal{W}_{\text{FH}} \mathbf{v}_1) + \phi_1 \frac{\partial \mathcal{W}_{\text{elas}}(\mathcal{F})}{\partial \mathcal{F}} : (\nabla \mathbf{v}_1 \mathcal{F}) d\mathbf{x}. \end{aligned} \quad (2.30)$$

Here, we do not *define* \dot{U} as in the first two lines; the “.” symbol and the partial derivative symbol are only notations that are replaced by spatial derivatives from the kinematic relations (2.9), (2.10) and (2.11). The term \dot{U} is only defined by the last line (2.30). It is important to point out that \dot{U} is linear in velocity.

Then, we define the functional

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

R is a function of the velocities. We want to find a set of velocities $\{\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_f\}$ that minimizes R , subject to the incompressibility condition (2.12) and (2.14). We thus consider

$$\mathcal{R} = R - \int_{\Omega_t} p \nabla \cdot (\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) d\mathbf{x} - \int_{\mathcal{R}_t} p \nabla \cdot \mathbf{v}_f d\mathbf{x}, \quad (2.31)$$

where p is the Lagrange multiplier, which will be identified as the mechanical pressure. To minimize \mathcal{R} , we take the variational derivative of \mathcal{R} with respect to the velocities

$$\frac{\delta \mathcal{R}}{\delta \mathbf{v}_i} = 0 \quad \text{for } i = 1, 2, f. \quad (2.32)$$

Now we show that these conditions are equivalent to the force balance equations (2.22)($i = 1, 2$) and (2.23). Let $\mathcal{T}_{i,f}$ and $f_{i,f}$ be defined by (2.25)-(2.26). First, we use

(2.9),(2.20),(2.30) and apply Reynolds transport formula to get

$$\begin{aligned}
& \frac{d}{dt} \int_{\Omega_t} \mathcal{W}_{\text{FH}}(\phi_1) + \mathcal{W}_{\text{elas}}(\mathcal{F}) d\mathbf{x} \\
&= \int_{\Omega_t} \left(\mathcal{W}_{\text{FH}} - \phi_1 \frac{\partial \mathcal{W}_{\text{FH}}}{\partial \phi_1} \right) (\nabla \cdot \mathbf{v}_1) + \left(\phi_1 \frac{\partial \mathcal{W}_{\text{elas}}}{\partial \mathcal{F}} \mathcal{F}^T \right) : (\nabla \mathbf{v}_1) d\mathbf{x} \\
&= - \int_{\Omega_t} (\nabla \cdot \mathcal{T}_1^{\text{FH}} + \nabla \cdot \mathcal{T}_1^{\text{elas}}) \cdot \mathbf{v}_1 d\mathbf{x} + \int_{\Gamma_t} (\mathcal{T}_1^{\text{FH}} \mathbf{n} + \mathcal{T}_1^{\text{elas}} \mathbf{n}) \cdot \mathbf{v}_1 dS
\end{aligned} \tag{2.33}$$

and use (2.25) to get

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

for $i = 1, 2$ and for $i = f$ when the domain is replaced by \mathcal{R}_t . Integrating the pressure terms in (2.31) by parts, and using (2.24), it follows that

$$\begin{aligned}
\mathcal{R} &= \int_{\Omega_t} -(\nabla \cdot \mathcal{T}_1) \cdot \mathbf{v}_1 - (\nabla \cdot \mathcal{T}_2) \cdot \mathbf{v}_2 + \frac{1}{2} \kappa |\mathbf{v}_1 - \mathbf{v}_2|^2 + (\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) \cdot \nabla p d\mathbf{x} \\
&+ \int_{\mathcal{R}_t} -(\nabla \cdot \mathcal{T}_f) \cdot \mathbf{v}_f + \mathbf{v}_f \cdot \nabla p d\mathbf{x} + A,
\end{aligned} \tag{2.34}$$

where A stands for the integral of boundary terms

$$\begin{aligned}
A &= \int_{\Gamma_t} (\mathcal{T}_1 \mathbf{n}) \cdot \mathbf{v}_1 + (\mathcal{T}_2 \mathbf{n}) \cdot \mathbf{v}_2 - (\mathcal{T}_f \mathbf{n}) \cdot \mathbf{v}_f \\
&- p^+(\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) \cdot \mathbf{n} + p^-(\mathbf{v}_f \cdot \mathbf{n}) + \frac{1}{2} (\eta_{\perp} w^2 + \eta_{\parallel} |\mathbf{q}|^2) dS,
\end{aligned} \tag{2.35}$$

in which the indexes $\{+, -\}$ denote evaluations on the Ω_t side and \mathcal{R}_t side, respectively. It is clear (2.32) yields (2.22) and (2.23).

To derive boundary conditions (2.27)-(2.29), we substitute $\{\mathbf{v}_1 + \epsilon a, \mathbf{v}_2 + \epsilon b, \mathbf{v}_f + \epsilon c\}$ in place of $\{\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_f\}$, and take derivative with respect to ϵ and let $\epsilon = 0$. This gives

$$\begin{aligned}
\left. \frac{dA}{d\epsilon} \right|_{\epsilon=0} &= \int_{\Gamma_t} (\mathcal{T}_1 \mathbf{n} + \mathcal{T}_2 \mathbf{n} - \mathcal{T}_f \mathbf{n} + [p]) \cdot a + (\mathcal{T}_2 \mathbf{n}) \cdot (b - a) - (\mathcal{T}_f \mathbf{n}) \cdot (c - a) \\
&- \phi_2 p^+(b - a) \cdot \mathbf{n} + p^-(c - a) \cdot \mathbf{n} + \eta_{\perp} w \cdot (c - a)_{\perp} + \eta_{\parallel} q \cdot (c - a)_{\parallel} dS.
\end{aligned} \tag{2.36}$$

Apply (2.16) and (2.17), to get

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

Therefore, one can further simplify (2.36) and obtain

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

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

$$\begin{aligned} \mathcal{T}_1 \mathbf{n} + \mathcal{T}_2 \mathbf{n} - \mathcal{T}_f \mathbf{n} + [p] \mathbf{n} &= 0, \\ \mathbf{n} \cdot (\mathcal{T}_2 \mathbf{n}) - \phi_2 [p] - \phi_2 \mathbf{n} \cdot (\mathcal{T}_f \mathbf{n}) + \phi_2 \eta_\perp w &= 0, \\ (\mathcal{T}_2 \mathbf{n} - \mathcal{T}_f \mathbf{n})_\parallel + \eta_\parallel \mathbf{q} &= 0. \end{aligned}$$

The first and second equations above are (2.27) and (2.28), and (2.29) follows from

$$(\mathcal{T}_2 \mathbf{n} - \mathcal{T}_f \mathbf{n})_\parallel + \eta_\parallel \mathbf{q} = -(\mathcal{T}_1 \mathbf{n})_\parallel + \eta_\parallel \mathbf{q} = 0.$$

3. Polyelectrolyte gel model. Now consider a polyelectrolyte gel. In this case, the polymer network carries charge and soluble ions which diffuse in the solvent and surrounding fluid. Assume the polymer network carries a fixed charge density of ρ_p per unit volume of dry polymer phase. Without loss of generality, let $\rho_p < 0$ (as in many real applications). We assume there are N kinds of ions in the system, and let $c_k, k = 1, \dots, N$ be the concentrations, \mathbf{u}_k be the velocities, and z_k be the valences (e.g. 1 for Na^+ and -1 for Cl^-). The *kinematic relations* include the balances of each ion species in the solvent and in the outside fluid, respectively:

$$\frac{\partial(\phi_2 c_k)}{\partial t} + \nabla \cdot (\phi_2 c_k \mathbf{u}_k) = 0 \quad \text{in } \Omega_t; \quad (3.1)$$

$$\frac{\partial c_k}{\partial t} + \nabla \cdot (c_k \mathbf{u}_k) = 0 \quad \text{in } \mathcal{R}_t. \quad (3.2)$$

We assume electroneutrality throughout the domain, which is treated as *kinematic constraints*:

$$\phi_1 \rho_p + \phi_2 \sum_{k=1}^N q z_k c_k = 0 \quad \text{in } \Omega_t, \quad (3.3)$$

$$\sum_{k=1}^N q z_k c_k = 0 \quad \text{in } \mathcal{R}_t. \quad (3.4)$$

Here, q is the elementary charge. The situation when the system is not electroneutral will be handled in the appendix I. Taking the time derivative of (3.3) and (3.4) and using (3.1) and (3.2), we obtain:

$$\rho_p \nabla \cdot (\phi_1 \mathbf{v}_1) + \sum_{k=1}^N q z_k \nabla \cdot (\phi_2 c_k \mathbf{u}_k) = 0 \quad \text{in } \Omega_t, \quad (3.5)$$

$$\sum_{k=1}^N q z_k \nabla \cdot (c_k \mathbf{u}_k) = 0 \quad \text{in } \mathcal{R}_t. \quad (3.6)$$

For reasons similar to the discussion following equation (2.14), it is more convenient to use (3.5) and (3.6) for our purposes. The boundary conditions include the continuities of ion flux across the interface

$$j_k := \phi_2 c_k^+ (\mathbf{u}_k^+ - \mathbf{v}_1) \cdot \mathbf{n} = c_k^- (\mathbf{u}_k^- - \mathbf{v}_1) \cdot \mathbf{n}, \quad (3.7)$$

and no flux across the outer boundary $\partial\mathcal{U}$,

$$\mathbf{u}_k \cdot \mathbf{n} = 0. \quad (3.8)$$

The total energy is the sum of elastic, Flory-Huggins and the entropic free energy of ions

$$\mathcal{U} = U + E_{\text{ion}} = U + \int_{\Omega_t} \phi_2 \mathcal{W}_{\text{ion}}(c_k) d\mathbf{x} + \int_{\mathcal{R}_t} \mathcal{W}_{\text{ion}}(c_k) d\mathbf{x}. \quad (3.9)$$

The forms of these energies are given by (2.19) and

$$\mathcal{W}_{\text{ion}} = k_B T \sum_{k=1}^N c_k \ln c_k, \quad (3.10)$$

in which $k_B T$ is the Boltzmann constant times absolute temperature. We always assume the temperature is constant in this paper. Let Rayleigh's dissipation function be

$$\begin{aligned} \mathcal{W} = W + \sum_{k=1}^N \int_{\Omega_t} \frac{1}{2} k_B T D_k^{-1} \phi_2^2 c_k |\mathbf{u}_k - \mathbf{v}_2|^2 d\mathbf{x} \\ + \sum_{k=1}^N \int_{\mathcal{R}_t} \frac{1}{2} k_B T D_k^{-1} c_k |\mathbf{u}_k - \mathbf{v}_f|^2 d\mathbf{x}, \end{aligned} \quad (3.11)$$

in which W is defined in (2.21). The two integrals represent frictional dissipation between ions and the solvent/outside fluid, and the coefficients $k_B T D_k^{-1}$ control the magnitude of this dissipation. For the ion-solvent friction, D_k may depend on ϕ_2 . We shall see later that D_k 's are nothing other than the ionic diffusion coefficients. We do not consider the friction between ions, and the friction between ions and polymer network.

Given the above kinematic relations, kinematic constraints, energies and Rayleigh function, we are ready to derive dynamic equations and boundary conditions for polyelectrolyte gels. We list them here before applying Onsager's principle. We retain (2.22) and (2.23), but need to add electrostatic forces to $f_{i,f}$

$$\begin{aligned} \mathbf{f}_1 &= \mathbf{f}^{\text{fric}} + \mathbf{f}_1^{\text{elec}}, \quad \mathbf{f}_1^{\text{elec}} = -\phi_1 \rho_p \nabla \psi, \\ \mathbf{f}_2 &= -\mathbf{f}^{\text{fric}} + \mathbf{f}_2^{\text{elec}}, \quad \mathbf{f}_2^{\text{elec}} = -\sum_{k=1}^N \phi_2 q z_k c_k \nabla \psi = -\mathbf{f}_1^{\text{elec}}, \\ \mathbf{f}_f &= 0. \end{aligned} \quad (3.12)$$

Here, ψ is the electrostatic potential, and \mathbf{f}^{fric} comes from (2.26). The ionic velocities are given by

$$\mathbf{u}_k = \begin{cases} \mathbf{v}_2 - \frac{D_k}{\phi_2 k_B T} \left(\nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) + q z_k \nabla \psi \right) & \text{in } \Omega_t; \\ \mathbf{v}_f - \frac{D_k}{k_B T} \left(\nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) + q z_k \nabla \psi \right) & \text{in } \mathcal{R}_t. \end{cases} \quad (3.13)$$

The ion concentrations satisfy

$$\frac{\partial}{\partial t} (\phi_2 c_k) + \nabla \cdot (\mathbf{v}_2 \phi_2 c_k) = \nabla \cdot \left(\frac{D_k c_k}{k_B T} \nabla \mu_k \right), \quad (3.14)$$

$$\frac{\partial c_k}{\partial t} + \nabla \cdot (\mathbf{v}_f c_k) = \nabla \cdot \left(\frac{D_k c_k}{k_B T} \nabla \mu_k \right). \quad (3.15)$$

As for boundary conditions, we retain (2.27), (2.29), but modify (2.28) by including osmotic pressure:

$$\eta_{\perp} w = \Pi_{\perp} = \mathbf{n} \cdot (\mathcal{T}_f \mathbf{n}) - \mathbf{n} \cdot \left(\frac{\mathcal{T}_2}{\phi_2} \right) \mathbf{n} + [p] - k_B T \sum_{k=1}^N [c_k]. \quad (3.16)$$

Lastly, we propose continuity of the chemical potential for k -th ion

$$[\mu_k] = 0 \quad \text{on } \Gamma_t; \quad (3.17)$$

$$\mu_k = \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} + qz_k \psi = k_B T (\ln c_k + 1) + qz_k \psi. \quad (3.18)$$

Now we apply Onsager's variational principle to derive (2.22)-(2.23), (3.13)-(3.15), (2.27), (2.29), (3.16) and (3.17). Define the functional

$$R = \dot{U} + \mathcal{W} \quad (3.19)$$

R is a function of the velocities. We want to find a set $\{\mathbf{u}_1, \dots, \mathbf{u}_N, \mathbf{v}_{1,2,f}\}$ that minimizes R , subject to the incompressibility condition (2.12), (2.14), and the electroneutrality condition (3.5), (3.6). Accordingly, we consider

$$\begin{aligned} \mathcal{R} = & R - \int_{\Omega_t} p \nabla \cdot (\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) + \psi \left(\rho_p \nabla \cdot (\phi_1 \mathbf{v}_1) + qz_k \sum_{k=1}^N \nabla \cdot (\phi_2 c_k \mathbf{u}_k) \right) d\mathbf{x} \\ & - \int_{\mathcal{R}_t} p \nabla \cdot \mathbf{v}_f + \psi \left(qz_k \sum_{k=1}^N \nabla \cdot (\phi_2 c_k \mathbf{u}_k) \right) d\mathbf{x} \end{aligned} \quad (3.20)$$

instead of R . As in the previous section, p is the Lagrange multiplier associated with incompressibility, and will be identified as the mechanical pressure; ψ is the Lagrange multiplier associated with electroneutrality, and will be identified as the electrostatic potential. We consider the variational derivatives with respect to velocities:

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

Now we prove (2.22)($i = 1, 2$), (2.23) and (3.14), (3.15) can be derived from the equalities above.

First, we calculate \dot{U} in Ω_t . For ionic energy, we differentiate the energy form and use (3.1),(3.2) to replace the time derivatives of u_k :

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

$$\begin{aligned}
&= \sum_{k=1}^N \int_{\Omega_t} \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot (\phi_2 c_k \mathbf{u}_k) - \phi_2 \nabla \left(c_k \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot \mathbf{v}_2 + \phi_2 \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \nabla c_k \cdot \mathbf{v}_1 \\
&\quad - \phi_2 \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \nabla c_k \cdot (\mathbf{v}_1 - \mathbf{v}_2) d\mathbf{x} + \int_{\Gamma_t} \sum_{k=1}^N \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \phi_2 c_k (\mathbf{v}_2 - \mathbf{u}_k) \cdot \mathbf{n} + \mathcal{W}_{\text{ion}} \phi_2 (\mathbf{v}_1 - \mathbf{v}_2) \cdot \mathbf{n} dS \\
&= \sum_{k=1}^N \int_{\Omega_t} \phi_2 c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot \mathbf{u}_k - k_B T \phi_2 \nabla c_k \cdot \mathbf{v}_2 d\mathbf{x} \\
&\quad + k_B T \sum_{k=1}^N \int_{\Gamma_t} \phi_2 c_k \ln c_k (\mathbf{v}_1 - \mathbf{u}_k) \cdot \mathbf{n} + \phi_2 c_k (\mathbf{v}_2 - \mathbf{u}_k) \cdot \mathbf{n} dS \tag{3.21}
\end{aligned}$$

Similarly for \mathcal{R}_t , we get

$$\begin{aligned}
&\frac{d}{dt} \int_{\mathcal{R}_t} \mathcal{W}_{\text{ion}} d\mathbf{x} \\
&= \sum_{k=1}^N \int_{\mathcal{R}_t} c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot \mathbf{u}_k d\mathbf{x} + k_B T \sum_{k=1}^N \int_{\Gamma_t} c_k \ln c_k (\mathbf{u}_k - \mathbf{v}_1) \cdot \mathbf{n} + c_k (\mathbf{u}_k \cdot \mathbf{n}) dS \\
&= \sum_{k=1}^N \int_{\mathcal{R}_t} c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot \mathbf{u}_k d\mathbf{x} \\
&\quad + k_B T \sum_{k=1}^N \int_{\Gamma_t} c_k \ln c_k (\mathbf{u}_k - \mathbf{v}_1) \cdot \mathbf{n} + c_k (\mathbf{u}_k - \mathbf{v}_f) \cdot \mathbf{n} + c_k (\mathbf{v}_f \cdot \mathbf{n}) dS \\
&= \sum_{k=1}^N \int_{\mathcal{R}_t} c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot \mathbf{u}_k - k_B T \nabla c_k \cdot \mathbf{v}_f d\mathbf{x} \\
&\quad + k_B T \sum_{k=1}^N \int_{\Gamma_t} c_k \ln c_k (\mathbf{u}_k - \mathbf{v}_1) \cdot \mathbf{n} + c_k (\mathbf{u}_k - \mathbf{v}_f) \cdot \mathbf{n} dS, \tag{3.22}
\end{aligned}$$

where the integral on the outside boundary vanishes, due to (3.8). Adding (3.21) and (3.22), we have

$$\begin{aligned}
&\frac{d}{dt} \int_{\Omega_t} \phi_2 \mathcal{W}_{\text{ion}} d\mathbf{x} + \frac{d}{dt} \int_{\mathcal{R}_t} \mathcal{W}_{\text{ion}} d\mathbf{x} \\
&= \sum_{k=1}^N \int_{\Omega_t} \phi_2 c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot \mathbf{u}_k - k_B T \phi_2 \nabla c_k \cdot \mathbf{v}_2 d\mathbf{x} \\
&\quad + \sum_{k=1}^N \int_{\mathcal{R}_t} c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot \mathbf{u}_k - k_B T \nabla c_k \cdot \mathbf{v}_f d\mathbf{x} \\
&\quad + k_B T \sum_{k=1}^N \int_{\Gamma_t} \phi_2 c_k^+ \ln c_k^+ (\mathbf{v}_1 - \mathbf{u}_k^+) \cdot \mathbf{n} + \phi_2 c_k^+ (\mathbf{v}_2 - \mathbf{u}_k^+) \cdot \mathbf{n} \\
&\quad + c_k^- \ln c_k^- (\mathbf{u}_k^- - \mathbf{v}_1) \cdot \mathbf{n} + c_k^- (\mathbf{u}_k^- - \mathbf{v}_f) \cdot \mathbf{n} dS. \tag{3.23}
\end{aligned}$$

On the other hand, the constraints in (3.20) can be simplified by

$$\int_{\Omega_t} \psi \frac{\partial}{\partial t} \left(\phi_1 \rho_p + \phi_2 \sum_{k=1}^N q z_k c_k \right) d\mathbf{x} + \int_{\mathcal{R}_t} \psi \frac{\partial}{\partial t} \left(\sum_{k=1}^N q z_k c_k \right) d\mathbf{x}$$

$$\begin{aligned}
&= \int_{\Omega_t} \psi \left(\frac{\partial \phi_1}{\partial t} \rho_p + \sum_{k=1}^N qz_k \frac{\partial(\phi_2 c_k)}{\partial t} \right) d\mathbf{x} + \int_{\mathcal{R}_t} \psi \left(\sum_{k=1}^N qz_k \frac{\partial c_k}{\partial t} \right) d\mathbf{x} \\
&= - \int_{\Omega_t} \psi \rho_p \nabla \cdot (\phi_1 \mathbf{v}_1) + \psi \sum_{k=1}^N qz_k \nabla \cdot (\phi_2 c_k \mathbf{u}_k) d\mathbf{x} - \int_{\mathcal{R}_t} \psi \left(\sum_{k=1}^N qz_k \nabla \cdot (c_k \mathbf{u}_k) \right) d\mathbf{x} \\
&= \int_{\Omega_t} \phi_1 \rho_p \nabla \psi \cdot \mathbf{v}_1 + \phi_2 \sum_{k=1}^N qz_k c_k \nabla \psi \cdot \mathbf{u}_k d\mathbf{x} + \int_{\mathcal{R}_t} \sum_{k=1}^N qz_k c_k \nabla \psi \cdot \mathbf{u}_k d\mathbf{x} \\
&\quad - \int_{\Gamma_t} \phi_1 \rho_p \psi^+ (\mathbf{v}_1 \cdot \mathbf{n}) + \phi_2 \sum_{k=1}^N qz_k c_k \psi^+ (\mathbf{u}_k^+ \cdot \mathbf{n}) - \sum_{k=1}^N qz_k c_k \psi^- (\mathbf{u}_k^- \cdot \mathbf{n}) dS \quad (3.24)
\end{aligned}$$

where (3.1) and (3.2) are used on the second line, (3.8) are used on the last line. Moreover,

$$\begin{aligned}
&- \int_{\Omega_t} p \nabla \cdot (\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) d\mathbf{x} - \int_{\mathcal{R}_t} p \nabla \cdot \mathbf{v}_f d\mathbf{x} \\
&= \int_{\Omega_t} (\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) \cdot \nabla p d\mathbf{x} + \int_{\mathcal{R}_t} \mathbf{v}_f \cdot \nabla p d\mathbf{x} + \int_{\Gamma_t} -p^+ (\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) \cdot \mathbf{n} + p^- (\mathbf{v}_f \cdot \mathbf{n}) dS. \quad (3.25)
\end{aligned}$$

Recalling (3.9)-(3.20), we now collect (3.23)-(3.25) and (2.34)-(2.35) to derive:

$$\begin{aligned}
\mathcal{R} &= \int_{\Omega_t} -(\nabla \cdot \mathcal{T}_1) \cdot \mathbf{v}_1 - (\nabla \cdot \mathcal{T}_2) \cdot \mathbf{v}_2 + \sum_{k=1}^N \phi_2 c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot (\mathbf{u}_k - \mathbf{v}_2) \\
&\quad + \frac{1}{2} \kappa |\mathbf{v}_1 - \mathbf{v}_2|^2 + \sum_{k=1}^N \frac{1}{2} k_B T D_k^{-1} \phi_2^2 c_k |\mathbf{u}_k - \mathbf{v}_2|^2 + \phi_1 \rho_p \nabla \psi \cdot \mathbf{v}_1 \\
&\quad + \phi_2 \sum_{k=1}^N qz_k c_k \nabla \psi \cdot \mathbf{u}_k + (\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) \cdot \nabla p d\mathbf{x} \\
&\quad + \int_{\mathcal{R}_t} -(\nabla \cdot \mathcal{T}_f) \cdot \mathbf{v}_f + \sum_{k=1}^N c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot \mathbf{u}_k - \sum_{k=1}^N k_B T \nabla c_k \cdot \mathbf{v}_f \\
&\quad + \sum_{k=1}^N \frac{1}{2} k_B T D_k^{-1} c_k |\mathbf{u}_k - \mathbf{v}_f|^2 + \sum_{k=1}^N qz_k c_k \nabla \psi \cdot \mathbf{u}_k + \mathbf{v}_f \cdot \nabla p d\mathbf{x} \\
&\quad + \int_{\Gamma_t} -\phi_1 \rho_p \psi^+ (\mathbf{v}_1 \cdot \mathbf{n}) - \phi_2 \sum_{k=1}^N qz_k c_k \psi^+ (\mathbf{u}_k^+ \cdot \mathbf{n}) + \sum_{k=1}^N qz_k c_k \psi^- (\mathbf{u}_k^- \cdot \mathbf{n}) \\
&\quad + k_B T \sum_{k=1}^N \left(\phi_2 c_k^+ \ln c_k^+ (\mathbf{v}_1 - \mathbf{u}_k^+) \cdot \mathbf{n} + \phi_2 c_k^+ (\mathbf{v}_2 - \mathbf{u}_k^+) \cdot \mathbf{n} \right. \\
&\quad \left. + c_k^- \ln c_k^- (\mathbf{u}_k^- - \mathbf{v}_1) \cdot \mathbf{n} + c_k^- (\mathbf{u}_k^- - \mathbf{v}_f) \cdot \mathbf{n} \right) dS + A \text{ in (2.35)}. \quad (3.26)
\end{aligned}$$

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 :

$$0 = \frac{\delta \mathcal{R}}{\delta \mathbf{u}_k} = \begin{cases} k_B T D_k^{-1} \phi_2^2 c_k (\mathbf{u}_k - \mathbf{v}_2) + \phi_2 c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) + \phi_2 qz_k c_k \nabla \psi & \text{in } \Omega_t; \\ k_B T D_k^{-1} c_k (\mathbf{u}_k - \mathbf{v}_f) + c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) + qz_k c_k \nabla \psi & \text{in } \mathcal{R}_t. \end{cases}$$

Therefore, we derive (3.13) and from (3.1) and (3.2) we derive (3.14) and (3.15). For \mathbf{v}_1 ,

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

and thus (2.22)($i = 1$) follows. For \mathbf{v}_2 ,

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

Apply (3.13) to derive (2.22)($i = 2$). For \mathbf{v}_f ,

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

Apply (3.13) to derive (2.23).

Lastly, we turn to the boundary terms. From (3.26), the boundary integrals are

$$\begin{aligned} & A + \int_{\Gamma_t} -\phi_1 \rho_p \psi^+ (\mathbf{v}_1 \cdot \mathbf{n}) - \sum_{k=1}^N q z_k \phi_2 c_k^+ \psi^+ (\mathbf{u}_k^+ \cdot \mathbf{n}) + \sum_{k=1}^N q z_k c_k^- \psi^- (\mathbf{u}_k^- \cdot \mathbf{n}) \\ & + k_B T \sum_{k=1}^N \left(\phi_2 c_k^+ \ln c_k^+ (\mathbf{v}_1 - \mathbf{u}_k^+) \cdot \mathbf{n} + \phi_2 c_k^+ (\mathbf{v}_2 - \mathbf{u}_k^+) \cdot \mathbf{n} + c_k^- \ln c_k^- (\mathbf{u}_k^- - \mathbf{v}_1) \cdot \mathbf{n} + c_k^- (\mathbf{u}_k^- - \mathbf{v}_f) \cdot \mathbf{n} \right) dS \\ = & A + \int_{\Gamma_t} \sum_{k=1}^N q z_k \phi_2 c_k^+ \psi^+ (\mathbf{v}_1 - \mathbf{u}_k^+) \cdot \mathbf{n} + \sum_{k=1}^N q z_k c_k^- \psi^- (\mathbf{u}_k^- - \mathbf{v}_1) \cdot \mathbf{n} \\ & + k_B T \sum_{k=1}^N \left(-[\ln c_k] \cdot j_k + \phi_2 c_k^+ (\mathbf{v}_2 - \mathbf{v}_1) \cdot \mathbf{n} + \phi_2 c_k^+ (\mathbf{v}_1 - \mathbf{u}_k^+) \cdot \mathbf{n} + c_k^- (\mathbf{u}_k^- - \mathbf{v}_1) \cdot \mathbf{n} + c_k^- (\mathbf{v}_1 - \mathbf{v}_f) \cdot \mathbf{n} \right) dS \\ = & A + \int_{\Gamma_t} \sum_{k=1}^N \left(-[q z_k \psi] \cdot j_k - [k_B T \ln c_k] \cdot j_k \right) + k_B T \sum_{k=1}^N \left(\phi_2 c_k^+ (\mathbf{v}_2 - \mathbf{v}_1) + c_k^- (\mathbf{v}_1 - \mathbf{v}_f) \cdot \mathbf{n} \right) dS \\ = & A + \int_{\Gamma_t} \sum_{k=1}^N \left(-[\mu_k] \cdot j_k + k_B T [c_k] \cdot w \right) dS \end{aligned}$$

Now, similar to the calculations in the mechanical case, it is easy to obtain the boundary conditions (2.27), (2.29), (3.16) and (3.17). Thus, we have derived all the equations and boundary conditions using Onsager's principle.

The case when the electroneutrality condition (3.3) and (3.4) is replaced by the Poisson equation (A.1) is treated in Appendix A. This requires the introduction of interface conditions (A.2) for the electrostatic potential. The energy function, upon which the variational principle is based, now includes the electrostatic energy (A.5). A similar calculation using Onsager's variational principle then leads to the system of dynamic equations as well as the boundary conditions. The main difference in the results between the electroneutral case above and the Poisson case is the presence of the Maxwell stress in the stress balance condition as well as the Helmholtz force, arising from possible spatial variations in the dielectric. We also point out that condition (3.16) in the electroneutral case reverts back to (2.28). We note that the

electroneutral treatment should be recovered from the Poisson treatment in the limit of zero Debye length. This limit was explored in [30]. We shall henceforth only deal with the electroneutral model since the Debye length is typically vanishingly small compared to the size of the system of interest.

4. Stability analysis of nonionic model, one-dimensional case. In this section, we consider the swelling dynamics of a one-dimensional gel without ions. Our goals are to find steady state solutions, to find the minimum decay rate of small perturbations, and to discuss the behavior 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 . Since it is one spatial dimension, 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 is convex. More precisely,

$$f''(\phi_1) = \frac{d^2 f}{d\phi_1^2} > 0. \quad (4.1)$$

and

$$\frac{d}{d\phi_1} \left(\frac{f(\phi_1)}{\phi_1} \right) \Big|_{\phi_1=0^+} < 0, \quad \frac{d}{d\phi_1} \left(\frac{f(\phi_1)}{\phi_1} \right) \Big|_{\phi_1=1^-} > 0 \quad (4.2)$$

which indicates the total free energy increases when the gel is exceedingly stretched or compressed. The constitutive equations (2.11)-(2.14), (2.22)-(2.24) and boundary conditions (2.15)-(2.18), (2.27)-(2.29) are as follows.

At $x = 0$,

$$v_1 = v_2 = 0. \quad (4.3a)$$

In $(0, a)$,

$$\phi_1 + \phi_2 = 1, \quad (4.3b)$$

$$\frac{\partial \phi_i}{\partial t} + (v_i \phi_i)_x = 0 \quad \text{for } i = 1, 2, \quad (4.3c)$$

$$(\phi_1 v_1 + \phi_2 v_2)_x = 0, \quad (4.3d)$$

$$(\eta_1 v_{1,x})_x + (f - \phi_1 f')_x - \phi_1 p_x + \kappa(v_2 - v_1) = 0, \quad (4.3e)$$

$$(\eta_2 v_{2,x})_x - \phi_2 p_x + \kappa(v_1 - v_2) = 0. \quad (4.3f)$$

At $x = a$

$$v_f - v_1 = \phi_2(v_2 - v_1), \quad (4.3g)$$

$$\eta_f(v_f)_x - \eta_1(v_1)_x - (f - \phi_1 f') - \eta_2(v_2)_x + [p] = 0, \quad (4.3h)$$

$$\eta_\perp(v_f - v_1) = \eta_f(v_f)_x - \phi_2^{-1} \eta_2(v_2)_x + [p], \quad (4.3i)$$

In (a, L) ,

$$(v_f)_x = 0, \quad (4.3j)$$

$$(\eta_f v_{f,x})_x - p_x = 0, \quad (4.3k)$$

At $x = L$

$$v_f = 0. \quad (4.3l)$$

Moreover,

$$\dot{a} = v_1(x = a). \quad (4.3m)$$

Note also that (2.17) and (2.29) becomes trivial in the one-dimensional case.

We first consider the equations for the surrounding fluid. From (4.3j) and (4.3l) it follows that $v_f \equiv 0$ in (a, L) , and from (4.3k) p is constant in (a, L) . We thus set $p = 0$ in (a, L) . Since in the outside fluid v_f and p are trivial, we may restrict our focus on the domain of gel $[0, a]$ from now on.

From (4.3b), (4.3d) and (4.3g), it follows that

$$\phi_1 v_1 + \phi_2 v_2 = 0 \quad \text{in } (0, a), \quad \text{or} \quad v_2 = -\frac{\phi_1 v_1}{1 - \phi_1}. \quad (4.4)$$

Adding (4.3e) and (4.3f) and integrating in x , it follows that

$$p = \eta_1 (v_1)_x + \eta_2 (v_2)_x + (f - \phi_1 f') + g(t) \quad \text{in } (0, a), \quad (4.5)$$

and $g(t) \equiv 0$ from (4.3h). Together with $\phi_2 = 1 - \phi_1$, we derive the following equations for $\{\phi_1, v_1\}$ in $(0, a)$:

$$\begin{aligned} \frac{\partial \phi_1}{\partial t} + (\phi_1 v_1)_x &= 0; \\ (1 - \phi_1)(\eta_1 v_{1,x})_x + \phi_1 \left(\eta_2 \left(\frac{\phi_1 v_1}{1 - \phi_1} \right)_x \right)_x + (1 - \phi_1)(f - \phi_1 f')_x &= \frac{\kappa v_1}{1 - \phi_1}. \end{aligned} \quad (4.6)$$

The boundary conditions are

$$\begin{aligned} v_1 &= 0 \quad \text{at} \quad x = 0, \\ -\eta_{1\perp} v_1 &= \eta_1 (v_1)_x + \frac{\phi_1}{1 - \phi_1} \eta_2 \left(\frac{\phi_1 v_1}{1 - \phi_1} \right)_x + (f - \phi_1 f') \quad \text{at} \quad x = a, \\ \dot{a} &= v_1(x = a). \end{aligned} \quad (4.7)$$

4.1. Steady state solutions. At steady state, all time derivatives vanish. Let $(\phi_1)_t = 0$ in (4.6)₁. Then $v_1 \equiv 0$ due to (4.7)₁, and (4.6)₂ reduces to

$$(f(\phi_1) - \phi_1 f'(\phi_1))_x = -\phi_1 (\phi_1)_x f''(\phi_1) = 0, \quad 0 < \phi_1(x) < 1.$$

Since our energy density function $f(\phi_1)$ is assumed strictly convex (4.1) 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 (4.5), namely

$$f(\phi_0) - \phi_0 f'(\phi_0) = 0. \quad (4.8)$$

It is easy to see there exists a unique solution to (4.8), from monotonicity of ϕ_1 and (4.2). Note that we made the tacit assumption that the gel does not swell to occupy the whole domain. That is, let $l_0 = \int_0^a \phi_1(x) dx$, we assume $L > l_0(\phi_0)^{-1}$.

This uniqueness of the steady state is to be expected on physical grounds; we have an isolated system with a convex free energy, and thus, there should be a unique state of thermodynamic equilibrium. It is also expected that this steady state is stable, and we examine this below.

4.2. Minimum decay rate near the equilibria. We start with equations (4.6) and boundary conditions (4.7) 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

$$x = \varphi_t(X) = X + \epsilon u(X, t) + O(\epsilon^2), \quad \epsilon \ll 1, \quad (4.9)$$

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 (2.10)

$$\begin{aligned} \phi_1 &= \phi_0 \left(\frac{\partial \varphi_t}{\partial X} \right)^{-1} = \phi_0 \left(1 - \epsilon \frac{\partial u}{\partial X} \right) + O(\epsilon^2); \\ v_1 &= \frac{\partial x}{\partial t} = \epsilon \frac{\partial u}{\partial t} + O(\epsilon^2). \end{aligned} \quad (4.10)$$

Since $\partial/\partial X = \partial/\partial x \cdot (1 + \epsilon u_X)$, we linearize (4.6) under the current configuration, and derive the equation involving only $O(\epsilon)$ terms as

$$H u_{txx} + \phi_0^2 f''(\phi_0) u_{xx} = \frac{\kappa u_t}{(1 - \phi_0)^2}, \quad H = \eta_1 + \eta_2 \frac{\phi_0^2}{(1 - \phi_0)^2} \quad (4.11)$$

where H is the mixed viscosity coefficient. For the boundary conditions, we apply (4.10) to (4.7) at $x = \epsilon u(0, 0)$ and $x = a + \epsilon u(L, 0)$. Using Taylor expansion, we can find the approximate boundary conditions at $x = 0$ and $x = a$. The linearized boundary conditions are as follows:

$$\begin{aligned} u_t &= 0 \quad \text{or} \quad u = 0 \quad \text{at} \quad x = 0, \\ -\eta_\perp u_t &= H u_{tx} + \phi_0^2 f''(\phi_0) u_x \quad \text{at} \quad x = a. \end{aligned} \quad (4.12)$$

Equations (4.11)-(4.12) satisfy a linearized version of energy dissipation identity. Multiply (4.11) by u_t and integrate over $(0, a)$, and we have

$$\begin{aligned} &\frac{d}{dt} \left(\frac{1}{2} \phi_0^2 f''(\phi_0) \int_0^a u_x^2 dx \right) \\ &= -H \int_0^a (u_{tx})^2 dx - \frac{\kappa}{(1 - \phi_0)^2} \int_0^a u_t^2 dx - \eta_\perp u_t(a)^2. \end{aligned} \quad (4.13)$$

The energy law indicates that the steady state (4.8) is stable. Now we examine the relaxation rate. Write $u(x, t)$ as the infinite sum of eigenfunctions:

$$u(x, t) = \sum_k a_k e^{-\lambda_k t} \omega_k(x). \quad (4.14)$$

The eigenfunction ω_k with eigenvalue λ_k satisfies

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

$$-\lambda_k \eta_\perp \omega_k = (\lambda_k H - \phi_0^2 f''(\phi_0)) \omega'_k \quad \text{at } x = a.$$

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

$$\omega_k'' = 0, \quad \text{and } \omega_k' = 0, \quad (4.15)$$

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

$$\begin{aligned} M^2 &= -\frac{\lambda \kappa}{(1 - \phi_0)^2 (\lambda H - \phi_0^2 f''(\phi_0))}, \quad M > 0; \\ B &= -\frac{\lambda \eta_\perp}{\lambda H - \phi_0^2 f''(\phi_0)} > 0, \end{aligned} \quad (4.16)$$

and let

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

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

$$\cot(Ma) = \frac{B}{M} = \frac{(1 - \phi_0) \eta_\perp}{\sqrt{\kappa}} \cdot \sqrt{\frac{\lambda}{\phi_0^2 f''(\phi_0) - \lambda H}}. \quad (4.17)$$

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

THEOREM 4.1. *Let the perturbation function $u(x, t)$ be defined by (4.14) and $\lambda = \lambda_1$ be the smallest eigenvalue satisfying (4.17) where $M(\lambda)$ and $B(\lambda)$ are defined by (4.16). 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 $\eta_\perp \rightarrow 0$,

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

In particular, if $\eta_\perp = 0$ (fully permeable),

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

(ii) As $\eta_\perp \rightarrow \infty$, $\lambda_1 \rightarrow 0+$. In particular, if $\eta_\perp = \infty$ (fully impermeable), $\lambda_1 = 0$.

(iii) As $H \rightarrow 0$, (4.17) becomes

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

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

REMARK 4.1. In (i), let $\eta_\perp = 0$. We have

$$\lambda_1 = \frac{\phi_0^2 f''(\phi_0)}{\frac{4\kappa a^2}{(1 - \phi_0)^2 \pi^2} + H}. \quad (4.18)$$

This value can be treated as the principal eigenvalue of the polymer phase (PEP), and will be useful in the analysis of the polyelectrolyte gel model.

5. Stability analysis of ionic model, one-dimensional case. We continue the stability analysis on the one-dimensional model in this section, with ions coming into play. The gel lies in $x \in (0, a) \subset (0, L)$ and is fixed at $x = 0$. We use the same notations as in section 4, and the constitutive equations (2.11)-(2.12), (2.22)-(2.23), and boundary conditions (2.15)-(2.18), (2.27), (2.29) together with ionic equations (3.3)-(3.4), (3.14)-(3.15), boundary conditions (3.7)-(3.8), (3.16) and (3.17). We start the stability analysis by first introducing the primed dimensionless variables

$$\begin{aligned} x &= 1_L x', \quad D_k = D_0 D'_k, \quad t = \frac{1_L^2}{D_0} t', \quad c_k = c_0 c'_k, \quad \psi = \frac{k_B T}{q} \psi', \quad \rho_p = q c_0 \rho'_p, \\ \kappa &= 1_\kappa \kappa', \quad f = \frac{k_B T}{1_L^3} f', \end{aligned} \quad (5.1)$$

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 primed symbols are dropped for notational convenience. We now state the nondimensionalized equations.

At $x = 0$,

$$v_1 = v_2 = 0, \quad (5.2a)$$

$$u_k = v_2 - \frac{D_k}{\phi_2} \left(\frac{(c_k)_x}{c_k} + z_k \psi_x \right) = 0. \quad (5.2b)$$

In $(0, a)$,

$$\phi_1 + \phi_2 = 1, \quad (5.2c)$$

$$\frac{\partial \phi_1}{\partial t} + (v_1 \phi_1)_x = 0, \quad (5.2d)$$

$$(\phi_1 v_1 + \phi_2 v_2)_x = 0, \quad (5.2e)$$

$$(\eta_1 v_{1,x})_x + (f - \phi_1 f')_x - \phi_1 p_x - \phi_1 \rho_p \psi_x + \kappa (v_2 - v_1) = 0, \quad (5.2f)$$

$$(\eta_2 v_{2,x})_x - \phi_2 p_x - \left(\sum_{k=1}^N z_k \phi_2 c_k \right) \psi_x + \kappa (v_1 - v_2) = 0, \quad (5.2g)$$

$$\frac{\partial}{\partial t} (\phi_2 c_k) + (v_2 \phi_2 c_k)_x = (D_k (c_k)_x + D_k c_k z_k \psi_x)_x, \quad (5.2h)$$

$$\phi_1 \rho_p + \sum_{k=1}^N z_k \phi_2 c_k = 0. \quad (5.2i)$$

At $x = a$:

$$\dot{a} = v_1(x = a), \quad (5.2j)$$

$$v_f - v_1 = \phi_2 (v_2 - v_1), \quad (5.2k)$$

$$\eta_f (v_f)_x - \eta_1 (v_1)_x - (f - \phi_1 f') - \eta_2 (v_2)_x + [p] = 0, \quad (5.2l)$$

$$[\mu_k] = [\ln c_k + z_k \psi] = 0, \quad (5.2m)$$

$$[j_k] = [c_k] \cdot w - [D_k (c_k)_x + D_k c_k z_k \psi_x] = 0, \quad (5.2n)$$

$$\eta_\perp (v_f - v_1) = \eta_f (v_f)_x - \phi_2^{-1} \eta_2 (v_2)_x + [p] - \sum_{k=1}^N [c_k] \quad \text{at } x = a. \quad (5.2o)$$

In (a, L) ,

$$(v_f)_x = 0, \quad (5.2p)$$

$$(\eta_f v_{f,x})_x - p_x = 0, \quad (5.2q)$$

$$\frac{\partial c_k}{\partial t} + (v_f c_k)_x = (D_k(c_k))_x + D_k c_k z_k \psi_x, \quad (5.2r)$$

$$\sum_{k=1}^N z_k c_k = 0. \quad (5.2s)$$

At $x = L$:

$$v_f = 0, \quad (5.2t)$$

$$u_k = v_f - \frac{D_k}{c_k}(c_k)_x - D_k z_k \psi_x = 0, \quad (5.2u)$$

We first consider the fluid region. From (5.2p), (5.2q) and (5.2t),

$$v_f = 0 \text{ in } (a, L), \quad p = \text{const.}, \quad \phi_1 v_1 + \phi_2 v_2 = 0 \text{ in } (0, a). \quad (5.3)$$

The last identity comes from (5.2k). We assume $p = 0$ in (a, L) . Then, from (5.2f)-(5.2g) and boundary conditions (5.2l), we get

$$p = \eta_1(v_1)_x + \eta_2(v_2)_x + (f - \phi_1 f') \text{ in } (0, a). \quad (5.4)$$

Thereupon we rewrite system (5.2) as follows for $\{\phi_1, v_1, \psi, c_k\}$:

At $x = 0$,

$$v_1 = 0, \quad (5.5a)$$

$$(c_k)_x + z_k c_k \psi_x = 0. \quad (5.5b)$$

In $(0, a)$,

$$\frac{\partial \phi_1}{\partial t} + (v_1 \phi_1)_x = 0, \quad (5.5c)$$

$$(\eta_1 v_{1,x})_x + (f - \phi_1 f')_x + \frac{\phi_1}{1 - \phi_1} \left(\eta_2 \left(\frac{\phi_1 v_1}{1 - \phi_1} \right)_x \right)_x - \frac{\phi_1 \rho_p}{1 - \phi_1} \psi_x = \frac{\kappa v_1}{(1 - \phi_1)^2}, \quad (5.5d)$$

$$\frac{\partial}{\partial t} ((1 - \phi_1) c_k) - (v_1 \phi_1 c_k)_x = (D_k(c_k))_x + D_k c_k z_k \psi_x, \quad (5.5e)$$

$$\phi_1 \rho_p + \sum_{k=1}^N z_k \phi_2 c_k = 0. \quad (5.5f)$$

At $x = a$:

$$[c_k] \cdot v_1 + [D_k(c_k)]_x + D_k c_k z_k \psi_x = 0, \quad (5.5g)$$

$$[\ln c_k + z_k \psi] = 0, \quad (5.5h)$$

$$-\eta_1 v_1 = \frac{\phi_1 \eta_2}{1 - \phi_1} \left(\frac{\phi_1 v_1}{1 - \phi_1} \right)_x + \eta_1 (v_1)_x + (f - \phi_1 f') - \sum_{k=1}^N [c_k] \text{ at } x = a. \quad (5.5i)$$

In (a, L) ,

$$\frac{\partial c_k}{\partial t} = (D_k(c_k)_x + D_k c_k z_k \psi_x)_x, \quad (5.5j)$$

$$\sum_{k=1}^N z_k c_k = 0. \quad (5.5k)$$

At $x = L$:

$$(c_k)_x + c_k z_k \psi_x = 0. \quad (5.5l)$$

REMARK 5.1. We assume the diffusion coefficient D_k to be constant in the outside fluid; however, in the gel region D_k may depend on ϕ_1 . They are often assumed equal when $\phi_1 = 0$.

5.1. Steady state solution. We look for solutions of (5.5) when all time derivatives vanish. Like the mechanical case, we only consider that the gel does not expand to occupy the whole domain. The following theorem tells us as long as the length of domain is sufficiently long, this is guaranteed and there exists a unique steady state. This result is again to be expected on physical grounds. The proof of this fact, however, is somewhat more involved than the non-ionic case of Section 4.

THEOREM 5.1. Consider the system (5.5). Let the essential length of the polymer

$$l_0 = \int_0^a \phi_1(x) dx$$

and total ion amount ($k = 1, \dots, N$)

$$A_k = \int_0^a \phi_2 c_k(x) dx + \int_a^L c_k(x) dx$$

satisfy the neutrality constraint

$$\sum_{k=1}^N z_k A_k + \rho_p l_0 = 0. \quad (5.6)$$

Then there exists $L^* > 0$ depending on A_1, \dots, A_N, l_0 , such that if $L > L^*$, (5.5) has a unique steady state solution:

$$\phi_1 = \phi_0, \quad \psi = \begin{cases} \psi_0^+ & \text{in } (0, a); \\ \psi_0^- & \text{in } (a, L), \end{cases} \quad \text{and } c_k = \zeta_k \cdot e^{-z_k \psi}, \quad (5.7)$$

in which $1 > \phi_0 > 0$, ψ_0^+ , ψ_0^- , $\zeta_k > 0$ are constants, ζ_k determined by A_k . If we let $\psi_0^- = 0$, the solution (5.7) is unique.

Proof. Let $l = a$ be the current length. We choose and fix arbitrary initial data $\{A_1, \dots, A_N, l_0\}$ such that (5.6) is satisfied, and temporarily assume that at the equilibrium state, $l < L$.

Let $\phi_1 = \phi_1(x)$, $\psi = \psi(x)$, $c_k = c_k(x)$, and let all time derivatives vanish. Let $\psi = 0$ at $x = L$. From (5.5e), (5.5g), (5.5j) and (5.5l),

$$D_k(c_k)_x + D_k c_k z_k \psi_x = 0 \quad \text{hence } (c_k)_x + c_k z_k \psi_x = 0 \quad \text{in } (0, L). \quad (5.8)$$

Therefore,

$$c_k = \zeta_k e_k, \quad e_k := e_k(\psi) = e^{-z_k \psi}, \quad (5.9)$$

ζ_k being constant in $(0, L)$. It follows from (5.5k) that $\psi \equiv 0$ in (a, L) . To show ψ is constant in $(0, a)$, we let

$$\begin{aligned} g(\psi) &= -\sum_{k=1}^N z_k c_k = -\sum_{k=1}^N z_k \zeta_k e_k, \\ g'(\psi) &= \sum_{k=1}^N z_k^2 \zeta_k e_k > 0. \end{aligned} \quad (5.10)$$

Now from (5.5f), $\phi_1 = \frac{g}{\rho_p + g}$, and (5.5d) becomes

$$\phi_1 \rho_p \left(f''(\phi_1) \cdot \frac{g'(\psi)}{(\rho_p + g(\psi))^2} + \frac{1}{1 - \phi_1} \right) \psi_x = 0. \quad (5.11)$$

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

$$((L - l) \cdot 1 + l \cdot (1 - \phi_1) e_k) \zeta_k = A_k, \quad \text{or} \quad \zeta_k = \frac{A_k}{L - l + l(1 - \phi_1) e_k}, \quad (5.12)$$

and (5.5) is reduced to

$$f(\phi_1) - \phi_1 f'(\phi_1) = \sum_{k=1}^N \frac{A_k (e_k - 1)}{L - l + l(1 - \phi_1) e_k}; \quad (5.13)$$

$$\sum_{k=1}^N \frac{z_k A_k}{L - l + l(1 - \phi_1) e_k} = 0; \quad (5.14)$$

$$l \phi_1 = l_0, \quad \phi_1 = \frac{g(\psi)}{\rho_p + g(\psi)}; \quad (5.15)$$

$$\sum_{k=1}^N z_k A_k + \rho_p l_0 = 0. \quad (5.16)$$

We use $e_k = e_k^+$ for short from now on, since $e_k^- \equiv 1$ is verified. Notice that $\rho_p < 0$, and $g(0) = -\sum_{k=1}^N \frac{z_k A_k}{L} = \frac{\rho_p l_0}{L} < 0$ from (5.16). Therefore, in (5.15), if $\psi = 0$,

$$l \phi_1 = l \cdot \frac{g(0)}{\rho_p + g(0)} = \frac{l \cdot l_0}{L + l_0} < l_0, \quad (5.17)$$

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

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

meaning in (5.14), as l increases, the solution for ψ increases, too. Finally, we turn to (5.13). With the convexity condition (4.1), it is easy to see that left hand side (LHS)

is strictly increasing in ψ . For the right hand side (RHS), it is strictly decreasing, due to

$$\begin{aligned}
& \frac{d}{d\psi} \sum_{k=1}^N \frac{A_k(e_k - 1)}{L - l + l(1 - \phi_1)e_k} \\
&= - \sum_{k=1}^N A_k \cdot \frac{z_k e_k L + (e_k - 1)^2 \frac{dl}{d\psi}}{(L - l + l(1 - \phi_1)e_k)^2} \\
&< - \sum_{k=1}^N A_k \cdot \frac{z_k e_k L}{(L - l + l(1 - \phi_1)e_k)^2} \quad (\text{since } \frac{dl}{d\psi} > 0) \\
&= - \sum_{k=1}^N \frac{A_k L}{L - l + l(1 - \phi_1)e_k} \cdot \frac{z_k e_k}{L - l + l(1 - \phi_1)e_k} \\
&< - \sum_{k=1}^N \frac{A_k L}{L - l + l(1 - \phi_1)e_k} \cdot \frac{z_k}{L - l_0} \quad (\text{since } \frac{z_k e_k}{L - l + l(1 - \phi_1)e_k} > \frac{z_k}{L - l_0} \quad \forall k) \\
&= - \frac{L}{L - l_0} \sum_{k=1}^N \frac{z_k A_k}{L - l + l(1 - \phi_1)e_k} = 0
\end{aligned} \tag{5.18}$$

the last equality comes from (5.14). Now if (5.13) has a solution, it is unique and the proof is over. Suppose this is not the case, which means that as ψ increases from $-\infty$ to some value $\psi^* < 0$, the gel stretches to occupy the whole domain ($l \nearrow L$, $\phi_1 \searrow \phi^* = l_0/L$) but in (5.13) LHS is still less than RHS. However, when $\psi = \psi^*$,

$$\text{RHS of (5.13)} = \frac{1}{L - l_0} \sum_{k=1}^N \frac{A_k(e_k - 1)}{e_k} \rightarrow 0 \text{ as } L \rightarrow \infty,$$

while as $L \rightarrow \infty$, $\phi^* \rightarrow 0$ and LHS has a positive limit (may be $+\infty$), due to (4.2). This indicates that if L is sufficiently large, the equality of (5.13) can be reached before ψ increases to ψ^* . We let the critical value be L^* and the conclusion follows.

□ We point out that

We rewrite (5.13)-(5.15) for convenient referrals:

$$f(\phi_0) - \phi_1 f'(\phi_0) = \sum_{k=1}^N \zeta_k (e_k - 1); \tag{5.19}$$

$$\sum_{k=1}^N z_k \zeta_k = 0; \tag{5.20}$$

$$\phi_0 = \frac{g(\psi_0)}{\rho_p + g(\psi_0)}, \quad g(\psi_0) = - \sum_{k=1}^N z_k \zeta_k e_k, \quad \text{or } \rho_p = - \frac{1 - \phi_0}{\phi_0} \sum_{k=1}^N z_k \zeta_k e_k. \tag{5.21}$$

We always assume $L > L^*$ from now on.

Consider a small perturbation of the system (5.5) near the equilibrium defined by (5.7), (5.19)-(5.21)

$$x = \varphi_t(X) = X + \epsilon u(X, t) + o(\epsilon), \quad \epsilon \ll 1, \tag{5.22}$$

$$\begin{aligned} c_k &= \zeta_k e^{-z_k \psi_0 + \epsilon z_k d_k} + o(\epsilon) \\ &= \zeta_k e_k (1 + \epsilon z_k d_k) + o(\epsilon), \end{aligned} \quad (5.23)$$

$$\psi = \psi_0 + \epsilon \psi_1 + o(\epsilon), \quad (5.24)$$

in which we used $e^{\epsilon \tau} = 1 + \epsilon \tau + o(\epsilon)$. Similar to (4.9), we have (4.10). Applying (5.22), (5.23) and (5.24) to the system (5.5), and using (5.7), (5.19)-(5.21), we derive the following linearized system of equations and boundary conditions for $\{u, d_k, \psi_1\}$.

At $x = 0$:

$$u = 0, \quad (d_k^+ + \psi_1^+)_x = 0. \quad (5.25a)$$

In $(0, a)$,

$$H u_{txx} + \phi_0^2 f''(\phi_0) u_{xx} = \frac{\kappa}{(1 - \phi_0)^2} u_t + \frac{\phi_0 \rho_p}{1 - \phi_0} (\psi_1^+)_x, \quad (5.25b)$$

$$\frac{\partial d_k^+}{\partial t} = \frac{D_k^+}{1 - \phi_0} (d_k^+ + \psi_1^+)_{xx}, \quad (5.25c)$$

$$\sum_{k=1}^N z_k^2 \zeta_k e_k^+ d_k^+ = \frac{\phi_0 \rho_p}{(1 - \phi_0)^2} u_x. \quad (5.25d)$$

At $x = a$:

$$u_t (e_k^+ - e_k^-) + z_k [D_k e_k (d_k + \psi_1)_x] = 0, \quad (5.25e)$$

$$[d_k + \psi_1] = 0, \quad (5.25f)$$

$$-\eta_{\perp} u_t = H u_{tx} + \phi_0^2 f''(\phi_0) u_x - \sum_{k=1}^N z_k \zeta_k [e_k d_k] \quad \text{at } x = a. \quad (5.25g)$$

In (a, L) ,

$$\frac{\partial d_k^-}{\partial t} = D_k^- (d_k^- + \psi_1^-)_{xx}, \quad (5.25h)$$

$$\sum_{k=1}^N z_k^2 \zeta_k e_k^- d_k^- = 0. \quad (5.25i)$$

At $x = L$:

$$(d_k^- + \psi_1^-)_x = 0. \quad (5.25j)$$

In (5.25b) and (5.25g), $H = \eta_1 + \phi_0^2 (1 - \phi_0)^{-2} \eta_2$ stands for the viscosity coefficient of the mixture. ϕ_0, ψ_0 are steady state solutions satisfying (5.19)-(5.21).

REMARK 5.2. *For convenience of computations hereafter, we use notations defined in (5.22)-(5.24). If one lets $c_k = c_{k,0} + \epsilon c_{k,1} + o(\epsilon)$, then (5.25c) and (5.25d) become*

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

and similarly for the other equations.

REMARK 5.3. If $H = 0$ in (5.25b), differentiate w.r.t. x and let $d_p = u_x$, d_p satisfies

$$\frac{\partial d_p}{\partial t} = A_1(d_p)_{xx} + A_2(\psi_1^+)_{xx},$$

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

This is similar to (5.25c), with “diffusion” coefficient A_1 . This indicates that under small perturbation, the polymer component behaves like a soluble anion species.

The system (5.25) also satisfies a linearized version of energy dissipation identity:

$$\begin{aligned} & \frac{d}{dt} \left(\frac{1}{2}\phi_0^2 f''(\phi_0) \int_0^a u_x^2 dx \right) + \frac{d}{dt} \left(\sum_{k=1}^N \frac{1}{2}(1-\phi_0)z_k^2\zeta_k e_k^+ \int_0^a (d_k^+)^2 dx \right) \\ & + \frac{d}{dt} \left(\sum_{k=1}^N \frac{1}{2}z_k^2\zeta_k e_k^- \int_a^L (d_k^-)^2 dx \right) = -H \int_0^a (u_{tx})^2 dx \\ & - \frac{\kappa}{(1-\phi_0)^2} \int_0^a u_t^2 dx - \sum_{k=1}^N z_k^2\zeta_k \int_0^L D_k e_k (d_k + \psi_1)_x^2 dx - \eta_\perp u_t(a)^2. \end{aligned} \quad (5.26)$$

We briefly sketch the proof here. Multiply (5.25b) by u_t and integrate by parts, and apply (5.25a), (5.25g) on the boundary terms. Multiply (5.25c) by $(1-\phi_0)z_k^2\zeta_k e_k^+(d_k^+ + \psi_1^+)$ and multiply (5.25h) by $z_k^2\zeta_k e_k^-(d_k^- + \psi_1^-)$ and integrate. Differentiate (5.25d) w.r.t. t and multiply by $(1-\phi_0)\psi_1^+$ and integrate, and similarly for (5.25i). Use (5.21) to replace ρ_p and add all the equations above. The boundary terms at $x = a$ will all vanish due to (5.25e)-(5.25f), except $\eta_\perp u_t^2$. The remaining terms exactly form (5.26).

The energy law indicates that the steady state obtained in this section is stable. It is of interest to examine the decay rate. We shall consider two cases: in section 5.2, ions in the outside fluid have infinite diffusion coefficients; in section 5.3, the gel is fully permeable, and there are two ion species in the system.

5.2. Minimum decay rate: uniform concentrations in (a, L) . A relatively simple case is when the outside fluid region is extremely long compared to the gel region ($L \gg a$) and the diffusion coefficients D_k^- 's are extremely large in it, such that we may assume the ions in (a, L) are uniformly distributed at any time $t \geq 0$, hence $d_k \equiv 0$, $\psi_1 \equiv 0$ in (a, L) . Let

$$u(x, t) = e^{-\lambda t} \tilde{u}(x), \quad \psi_1(x, t) = e^{-\lambda t} \tilde{\psi}_1(x), \quad d_k = e^{-\lambda t} \tilde{d}_k(x), \quad \text{and} \quad v(x) = -\tilde{u}_x(x). \quad (5.27)$$

Then from (5.25) we derive the following reduced system: in $(0, a)$,

$$(-\lambda H + \phi_0^2 f''(\phi_0))v_{xx} = -\frac{\lambda\kappa}{(1-\phi_0)^2}v + \frac{\phi_0\rho_p}{1-\phi_0}(\psi_1)_{xx}, \quad (5.28)$$

$$-\lambda d_k = \frac{D_k}{1-\phi_0}(d_k + \psi_1)_{xx}, \quad (5.29)$$

$$\sum_{k=1}^N z_k^2\zeta_k e_k d_k = -\frac{\phi_0\rho_p}{(1-\phi_0)^2}v, \quad (5.30)$$

while

$$(d_k + \psi_1)_x = 0, \quad x = 0, \quad (5.31)$$

$$d_k = 0, \quad \psi_1 = 0, \quad x = a \quad (5.32)$$

in which we have dropped the tildes for notational convenience. We first consider a perturbation for which $\psi_1 \equiv 0$ in $(0, a)$. This can only happen when

$$b = \frac{D_k}{(1 - \phi_0)\lambda} = \frac{(-\lambda H + \phi_0^2 f''(\phi_0))(1 - \phi_0)^2}{\lambda \kappa} \quad \forall k. \quad (5.33)$$

In the following we always rule out this special case and assume that not all D_k 's are equal. From boundary conditions, we may consider a single mode perturbation, letting $\psi_1 = \cos \omega(x - \alpha)$. The eigenvalues are characterized by the following theorem.

THEOREM 5.2. *Let $\{\lambda, v, d_k, \psi_1\}$ satisfy equations (5.28)-(5.32). The solutions of the following equations,*

$$\frac{\phi_0^2 \rho_p^2}{(1 - \phi_0)((\kappa + (1 - \phi_0)^2 H \omega^2)\lambda - \phi_0^2(1 - \phi_0)^2 f''(\phi_0)\omega^2)} + \sum_{k=1}^N \frac{D_k z_k^2 \zeta_k e_k}{(1 - \phi_0)\lambda - D_k \omega^2} = 0. \quad (5.34)$$

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 (5.28)-(5.32). Particularly, let λ_1 be the smallest solution of (5.34) among all ω 's, it satisfies the equation with $\omega = \frac{\pi}{2a}$. Furthermore, if we let

$$\gamma_1 = \min\left\{\frac{\phi_0^2 f''(\phi_0)}{\frac{4\kappa a^2}{(1 - \phi_0)^2 \pi^2} + H}, \frac{D_k \pi^2}{4(1 - \phi_0)a^2}, k = 1, \dots, N\right\}, \quad (5.35)$$

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

Proof. Let $\psi_1 = \cos \omega(x - \alpha)$. First, we have to show that resonance does not occur, or say

$$\lambda \neq \frac{\phi_0^2 f''(\phi_0)}{\frac{\kappa}{(1 - \phi_0)^2 \omega^2} + H}, \frac{D_k \omega^2}{1 - \phi_0}, k = 1, \dots, N. \quad (5.36)$$

Suppose $\lambda = \frac{D_k \omega^2}{1 - \phi_0}$, from (5.29), d_k contains $x \sin \omega(x - \alpha)$ term, but then (5.32) cannot hold. This means $\lambda \neq \frac{D_k \omega^2}{1 - \phi_0}$ for any $k = 1, \dots, N$ 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 (5.28), v contains $x \cos \omega(x - \alpha)$ term, but then (5.30) cannot hold.

Now from (5.28) and (5.29) we get

$$v = \frac{\phi_0(1 - \phi_0)\rho_p \omega^2}{((\kappa + (1 - \phi_0)^2 H \omega^2)\lambda - \phi_0^2(1 - \phi_0)^2 f''(\phi_0)\omega^2)} \cos \omega(x - \alpha); \quad (5.37)$$

$$d_k = \frac{D_k \omega^2}{(1 - \phi_0)\lambda - D_k \omega^2} \cos \omega(x - \alpha). \quad (5.38)$$

Apply the above equations to (5.30), we derive (5.34), which is of the following pattern:

$$\sum_{i=1}^M \frac{\alpha_i}{x - \beta_i} = 0, \quad \alpha_i, \beta_i > 0, \quad \beta_1 < \beta_2 < \cdots < \beta_M, \quad (5.39)$$

there are $M - 1$ roots each of which lies in (β_i, β_{i+1}) . For (5.34), the corresponding β_i 's are

$$\frac{\phi_0^2 f''(\phi_0)}{(1 - \phi_0)^2 \omega^2 + H}, \quad \frac{D_k \omega^2}{1 - \phi_0}, \quad k = 1, \dots, N. \quad (5.40)$$

From (5.31)-(5.32) 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 (5.35). Finally, we need to prove this λ_1 is the smallest root of (5.34) among all possible ω . In fact, we have

$$\frac{d\lambda_1}{d\omega} > 0. \quad (5.41)$$

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

Proof of (5.41). It is convenient to write (5.34) in the form

$$\sum_{k=1}^N \frac{\alpha_k}{\lambda_1 - \beta_k \omega^2} + \frac{1}{(1 + \alpha_0 \omega^2)\lambda_1 - \beta_0 \omega^2} = 0, \quad \alpha_0, \alpha_k, \beta_0, \beta_k > 0. \quad (5.42)$$

Differentiate to get

$$\begin{aligned} & \frac{d\lambda_1}{d\omega^2} \left(\sum_{k=1}^N \frac{\alpha_k}{(\lambda_1 - \beta_k \omega^2)^2} + \frac{1 + \alpha_0 \omega^2}{((1 + \alpha_0 \omega^2)\lambda_1 - \beta_0 \omega^2)^2} \right) \\ &= \sum_{k=1}^N \frac{\alpha_k \beta_k}{(\lambda_1 - \beta_k \omega^2)^2} - \frac{\alpha_0 \lambda_1 - \beta_0}{((1 + \alpha_0 \omega^2)\lambda_1 - \beta_0 \omega^2)^2}. \end{aligned} \quad (5.43)$$

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 (5.35), the smallest is a PEI. In this case,

$$\lambda_1 < \text{PEP} \quad \text{or} \quad (1 + \alpha_0 \omega^2)\lambda_1 - \beta_0 \omega^2 < 0, \quad \text{hence} \quad \alpha_0 \lambda_1 - \beta_0 < 0, \quad (5.44)$$

and hence the right hand side is positive. (ii) in (5.35), the smallest is the PEP. In this case, if $\alpha_0 \lambda_1 - \beta_0 < 0$, the proof is done. Otherwise,

$$\begin{aligned} & \sum_{k=1}^N \frac{\alpha_k \beta_k}{(\lambda_1 - \beta_k \omega^2)^2} - \frac{\alpha_0 \lambda_1 - \beta_0}{((1 + \alpha_0 \omega^2)\lambda_1 - \beta_0 \omega^2)^2} \\ &= \sum_{k=1}^N \frac{\alpha_k \beta_k}{(\lambda_1 - \beta_k \omega^2)^2} + \frac{\alpha_0 \lambda_1 - \beta_0}{(1 + \alpha_0 \omega^2)\lambda_1 - \beta_0 \omega^2} \cdot \frac{1}{(1 + \alpha_0 \omega^2)\lambda_1 - \beta_0 \omega^2} \\ &= \sum_{k=1}^N \frac{\alpha_k \beta_k}{(\lambda_1 - \beta_k \omega^2)^2} + \frac{\alpha_0 \lambda_1 - \beta_0}{((1 + \alpha_0 \omega^2)\lambda_1 - \beta_0 \omega^2)} \cdot \sum_{k=1}^N \frac{\alpha_k}{\lambda_1 - \beta_k \omega^2} \\ &= \sum_{k=1}^N \frac{\alpha_k}{\lambda_1 - \beta_k \omega^2} \left(\frac{\beta_k}{\lambda_1 - \beta_k \omega^2} + \frac{\alpha_0 \lambda_1 - \beta_0}{(1 + \alpha_0 \omega^2)\lambda_1 - \beta_0 \omega^2} \right) \end{aligned} \quad (5.45)$$

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

$$\frac{\beta_k}{\lambda_1 - \beta_k\omega^2} + \frac{\alpha_0\lambda_1 - \beta_0}{\lambda_1 + \alpha_0\omega^2\lambda_1 - \beta_0\omega^2} < \frac{\beta_k}{0 - \beta_k\omega^2} + \frac{\alpha_0\lambda_1 - \beta_0}{0 + \alpha_0\omega^2\lambda_1 - \beta_0\omega^2} = 0, \quad (5.46)$$

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

Notice the first term in (5.35) is the same as the PEP defined in Remark 4.1. The other terms correspond to the decay rates of the ion species when they are considered in isolation, 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. This result can be understood as an instance of the following well-known fact about the interlacing of eigenvalues of a symmetric matrix when one ‘‘constrains’’ the symmetric matrix to a proper subspace (see, for example, Chapter 1 of [23]). Suppose we have an $(N + 1) \times (N + 1)$ symmetric positive definite matrix A . The smallest eigenvalue λ_{\min} of A can be computed as follows:

$$\lambda_{\min} = \min_{\|\mathbf{x}\|=1} \langle A\mathbf{x}, \mathbf{x} \rangle, \quad \mathbf{x} \in \mathbb{R}^{N+1}. \quad (5.47)$$

Let \mathcal{P} be a N -dimensional subspace of \mathbb{R}^{N+1} and Q be the orthogonal projection on to this subspace. Then the smallest eigenvalue of $\widehat{\lambda}_{\min} Q^T A Q$ is given as follows:

$$\widehat{\lambda}_{\min} = \min_{\|\mathbf{x}\|=1, \mathbf{x} \in \mathcal{P}} \langle A\mathbf{x}, \mathbf{x} \rangle. \quad (5.48)$$

From this, it is easily seen that $\widehat{\lambda}_{\min}$ must be greater than λ_{\min} . It is possible to rewrite the above proof as an application of this fact. In particular, the N -dimensional subspace is that defined by the electroneutrality constraint. The fact that the minimum decay rate is larger than the minimum of the decay rates considered in isolation is then a direct consequence of this general fact.

For each ion species, there is a positive weight $D_k z_k^2 \zeta_k e_k$ measuring how much this ion species affects the eigenvalues in (5.34). 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 or small valence are more important than other ones. Furthermore, if we decrease one weight, say $D_j z_j^2 \zeta_j e_j$, 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 (5.19)-(5.21). While ρ_p changes, we assume the outside concentrations, namely ζ_k , are unchanged. View ϕ_0, ψ_0, λ as functions of ρ_p , and differentiate these quantities w.r.t. ρ_p to derive (we drop sub-indexes with no confusion)

$$\left. \frac{d\phi}{d\rho} \right|_{\rho=0} = 0, \quad \left. \frac{d\psi}{d\rho} \right|_{\rho=0} = \frac{\frac{\phi}{1-\phi} - \frac{\rho^2}{(1-\phi)^2 f''(\phi)}}{\sum_{k=1}^N z_k^2 \zeta_k e_k} = \frac{\phi}{1-\phi} \cdot \left(\sum_{k=1}^N z_k^2 \zeta_k e_k \right)^{-1} > 0, \quad (5.49)$$

and from (5.34)

$$\left. \frac{d\lambda}{d\rho} \right|_{\rho=0} = -\frac{\phi}{1-\phi} \cdot \sum_{k=1}^N \frac{D_k z_k^3 \zeta_k}{(1-\phi)\lambda - D_k \omega^2} \cdot \left(\sum_{k=1}^N z_k^2 \zeta_k \right)^{-1} \cdot \left(\sum_{k=1}^N \frac{D_k z_k^2 \zeta_k}{[(1-\phi)\lambda - D_k \omega^2]^2} \right)^{-1}. \quad (5.50)$$

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

$$S := -\sum_{k=1}^N \frac{D_k z_k^3 \zeta_k}{(1-\phi)\lambda - D_k \omega^2} = -\sum_{k=1}^N z_k \cdot \frac{D_k z_k^2 \zeta_k}{(1-\phi)\lambda - D_k \omega^2}, \quad (5.51)$$

since all other terms are positive. Recall γ_1 is the smallest of PEP and PEIs, defined by (5.35). At $\rho_p = 0$, if γ_1 is PEP, S has indefinite sign; if γ_1 is a PEI, there are two cases. Let $D_1 = \min\{D_1, \dots, D_N\}$ and for simplicity, we assume it is unique (if not, combine the weights). When $N = 2$, it is easily seen that $\text{sgn}(S) = -\text{sgn}(z_1)$; when $N > 2$, one might guess the same conclusion holds. If z_2, \dots, 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 (5.20), we may increase z_2 by $z_2 \mapsto h z_2$ and $\zeta_2 \mapsto h^{-1} \zeta_2$. When h is sufficiently large, the principal eigenvalue of (5.34) satisfies $\lambda_1 \approx (1-\phi)^{-1} D_1 \omega^2 + C h^{-1}$, 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 , and all other terms are bounded. Thus $S > 0$ 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 $\rho_p = 0$, γ_1 is PEP, since it is a singular point of (5.34), 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, the other ion species must be an anion and its concentration must increase, thus increasing 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.

5.3. Minimum decay rate: permeable gel with two ion species. Let $\mathbb{U} = (0, L)$, $\Omega = (0, a)$ and the gel be fixed at $x = 0$. We consider the case when ions diffuse in the outside fluid. However, we only deal with two ion species, and $\eta_{\perp} = 0$, since the algebraic complexity is complicated for $\eta_{\perp} \neq 0$ and increases drastically when $N > 2$. The perturbation variables $\{u, d_k, \psi_1\}$ are determined by (5.25). Let

$$u(x, t) = e^{-\lambda t} \tilde{u}(x), \quad \psi_1(x, t) = e^{-\lambda t} \tilde{\psi}_1(x), \quad d_k = e^{-\lambda t} \tilde{d}_k(x), \quad (5.52)$$

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

At $x = 0$:

$$u = 0, \quad (d_k^+ + \psi_1^+)_x = 0. \quad (5.53a)$$

In $(0, a)$,

$$(-\lambda H + \phi_0^2 f''(\phi_0)) u_{xx} = -\frac{\kappa \lambda}{(1-\phi_0)^2} u + \frac{\phi_0 \rho_p}{1-\phi_0} (\psi_1^+)_x, \quad (5.53b)$$

$$-\lambda d_k^+ = \frac{D_k^+}{1 - \phi_0} (d_k^+ + \psi_1^+)_{xx}, \quad D_k^+ = D_k^+(\phi_0), \quad (5.53c)$$

$$\sum_{k=1}^N z_k^2 \zeta_k e_k^+ d_k^+ = \frac{\phi_0 \rho_p}{(1 - \phi_0)^2} u_x. \quad (5.53d)$$

At $x = a$:

$$\lambda u (e_k^+ - e_k^-) = z_k [D_k e_k (d_k + \psi_1)_x], \quad (5.53e)$$

$$[d_k + \psi_1] = 0, \quad (5.53f)$$

$$(-\lambda H + \phi_0^2 f''(\phi_0)) u_x - \sum_{k=1}^N z_k \zeta_k [e_k d_k] = 0 \quad \text{at } x = a. \quad (5.53g)$$

In (a, L) ,

$$-\lambda d_k^- = D_k^- (d_k^- + \psi_1^-)_{xx}, \quad (5.53h)$$

$$\sum_{k=1}^N z_k^2 \zeta_k e_k^- d_k^- = 0. \quad (5.53i)$$

At $x = L$:

$$(d_k^- + \psi_1^-)_x = 0. \quad (5.53j)$$

We have dropped the tildes for notational convenience. Consider the case when there are only two ion species, namely $N = 2$. Let $z_1 > 0$ and $z_2 < 0$. Here we temporarily assume $H = 0$ to make the equations simpler. It will be seen later that the decay rate estimates are almost indifferent with or without the viscosities. Then (5.53b)-(5.53d) become

$$-\lambda u = A_1 u_{xx} + A_2 (\psi_1^+)_x, \quad (5.54)$$

$$-\lambda d_k^+ = B_k (d_k^+)_{xx} + B_k (\psi_1^+)_{xx}, \quad k = 1, 2, \quad (5.55)$$

$$C_1 d_1^+ + C_2 d_2^+ = -u_x := w, \quad (5.56)$$

in which

$$A_1 = \frac{f''(\phi_0) \phi_0^2 (1 - \phi_0)^2}{\kappa}, \quad A_2 = -\frac{\rho_p \phi_0 (1 - \phi_0)}{\kappa}, \quad (5.57)$$

$$B_k = \frac{D_k^+}{1 - \phi_0}, \quad C_k = -\frac{z_k^2 \zeta_k e_k^+ (1 - \phi_0)^2}{\phi_0 \rho_p}, \quad (5.58)$$

$$A_{1,2}, \quad B_{1,2}, \quad C_{1,2} > 0. \quad (5.59)$$

REMARK 5.4. *Looking at the linearized momentum equation (5.53b), the polymer phase satisfies a diffusion-type equation. Typically, the diffusion coefficient A_1 in (B.2) is much smaller than ionic diffusion coefficients D_k (see, such as [15]). An example can be found in [40] that $A_1 = 3.2 \times 10^{-7} \text{cm}^2/\text{s}$ and compared to NaCl in water, which has $D \approx 1.6 \times 10^{-5} \text{cm}^2/\text{s}$, it is much smaller.*

We state the main theorem about the principal eigenvalue λ_1 here. However, we will not present the long technical calculations in the main body. The details of the proof are found in Appendix B.

THEOREM 5.3. Let $\{u, d_{1,2}, \psi_1\}$ be perturbation variables from an equilibrium state defined by (5.7), satisfying (5.52)-(5.53j). Let λ_1 be the minimum decay rate in (5.52). Assume

$$\frac{f''(\phi_0)\phi_0^2(1-\phi_0)^2}{\kappa} \leq \frac{D_1^+}{1-\phi_0}, \frac{D_2^+}{1-\phi_0}, \quad (5.60)$$

then λ_1 can be bounded above by

$$\lambda_1 < \left(\frac{3\pi}{2}\right)^2 \cdot \min \left\{ \frac{D_1^+}{a^2(1-\phi_0)}, \frac{D_2^+}{a^2(1-\phi_0)}, \frac{D_z^-}{(L-a)^2} \right\}, \quad D_z^- = \frac{(|z_1| + |z_2|)D_1^- D_2^-}{(|z_1|D_1^- + |z_2|D_2^-)}. \quad (5.61)$$

If we further assume

$$D_1^+ \leq D_2^+, \quad (5.62)$$

then λ_1 can be bounded below by

$$\lambda_1 \geq \min \left\{ \frac{\phi_0^2 f''(\phi_0)}{\frac{4a^2\kappa}{\pi^2(1-\phi_0)^2} + H}, \frac{\pi^2}{4(L-a)^2} D_z^- \right\}. \quad (5.63)$$

The asymmetry in ionic species 1 and 2 in the statement of the lower bound estimate (see (5.62)) stems from our assumption $z_1 > 0$, $z_2 < 0$ and that the fixed charge density ρ_p is negative.

We first note that D_z^- above can be interpreted as the diffusion coefficient in the outside fluid region. Indeed, consider the equations (5.5j) and (5.5k) with $N = 2$. We may eliminate ψ and c_2 from these equations, to obtain a single equation for c_1 alone, which reads:

$$\frac{\partial c_1}{\partial t} = D_z^- \frac{\partial^2 c_1}{\partial x^2} \quad (5.64)$$

Under the electroneutrality constraint, therefore, the two ions behave as one solute with diffusion coefficient D_z^- .

We may now interpret the result of the above theorem as follows. When there are two ion species in the system, there are essentially four components under consideration: gel, anion in the polymer region, cation in the polymer region, and the ions in the fluid region. It is easy to see that

$$\frac{\pi^2}{4a^2} \cdot \frac{D_1^+}{1-\phi_0}, \quad \frac{\pi^2}{4a^2} \cdot \frac{D_2^+}{1-\phi_0}$$

correspond to the isolated ionic decay rates in the polymer region (corresponding to PEI in Section 5.2). As observed above, in the outside fluid region, the two ionic species act as one solute with diffusion coefficient D_z^- . Therefore, a reasonable expression for the isolated ionic decay rate in the outside fluid would be:

$$\frac{\pi^2}{4(L-a)^2} D_z^-. \quad (5.65)$$

Further, if we let $H = 0$, the first expression in (5.63) becomes

$$\frac{\pi^2}{4a^2} \cdot \frac{f''(\phi_0)\phi_0^2(1-\phi_0)^2}{\kappa}$$

which is the isolated polymer decay rate (corresponding to PEP in Section 5.2). The expressions in the right hand side of the upper bound estimate (5.61) are simply the second eigenvalues of each component. Theorem 5.3 states that the global decay rate must be slower than the fastest of the second modes and must be faster than the slowest of the first modes. The above result then, is an analogue of Theorem 5.2. The proof of this result, given in Appendix B, cannot, however, be interpreted simply in terms of interlacing of eigenvalues as was possible for Theorem 5.2 (see comment after its proof). In particular, we are unable to prove that the minimum eigenvalue lies exactly between the two slowest modes considered in isolation.

Do the estimates in Theorem 5.3 still hold if restrictions on the diffusion coefficients are removed, or $N > 2$? We conjecture, but have not been able to prove this for more general cases, due to the complexity in the algebraic expression of λ . In fact, it is physically intuitive to guess that λ is an increasing function with respect to every B_k and A_1 . If this is true, we can arrive at the following corollary:

COROLLARY 5.4. *If the principal global decay rate λ_1 is increasing with respect to A_1 , B_1 and B_2 , then $\lambda \geq$*

$$\min \left\{ \frac{\phi_0^2 f''(\phi_0)}{\frac{4a^2 \kappa}{\pi^2(1-\phi_0)^2} + H}, \frac{\pi^2 D_1^+}{4a^2(1-\phi_0)}, \frac{\pi^2 D_2^+}{4a^2(1-\phi_0)}, \frac{\pi^2 D_z^-}{4(L-a)^2} \right\} \quad (5.66)$$

Proof. Suppose the statement is not true. Then λ_1 is smaller than the minimum of the four candidates in (5.66) for some equilibrium state. Decrease A_1 and B_1 if necessary to make $A_1 \leq B_1 \leq B_2$, while maintain the minimum value in (5.66). Since λ_1 decreases during this procedure, the inequality still holds, which is a contradiction to Theorem 5.3. \square

The proof gives a clue to tackle the general case: if one can prove that λ_1 is an increasing function with respect to all the diffusion coefficients, and prove the estimates for one special situation, then all the others are clear by manipulation of the diffusion coefficients.

6. 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 total concentration of each ion is discretely conserved, which we have found to be crucial in maintaining electroneutrality of the computed solution. Maintenance of electroneutrality, in turn, has proved essential for a stable numerical scheme. Since electroneutrality is an algebraic constraint, we must use an implicit scheme for time-stepping, and we use a backward-Euler-type scheme for this purpose. To alleviate the difficulty of finding a good initial guess for Newton's method at the first time step, we first solve for the steady state solution and then iterate along a homotopy path to the current initial data. The details of this numerical scheme will be reported in a subsequent publication. 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 $t = 0^+$, 0.9, 9, 90, with

$$L = 5, \quad a = 3, \quad \eta_1 = 0.01, \quad \eta_2 = 0.02, \quad \eta_\perp = 0.01, \quad \kappa = 10, \quad \rho_p = -0.01, \\ z_1 = 1, \quad z_2 = -1, \quad D_1^- = 2, \quad D_2^- = 4, \quad D_{1,2}^+ = (1-\phi)D_{1,2}^-, \quad f(\phi) = \frac{1}{\phi(1.2-\phi)}$$

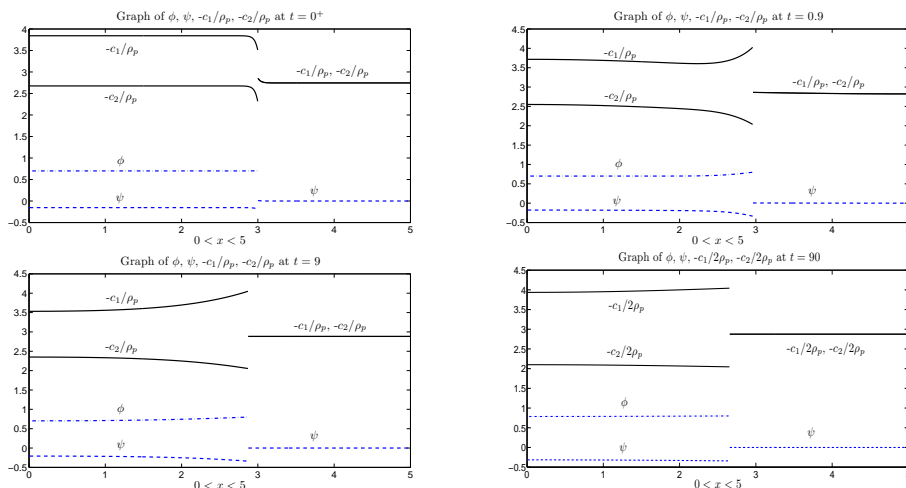


FIG. 6.1. Simulation with two ion species, the discontinuity occurs at the gel-fluid interface

and initial conditions

$$\begin{aligned} \phi_1 = 0.7, \quad c_1 = 0.077 & \quad \text{for } 0 < x < 3; \\ c_1 = 0.055 & \quad \text{for } 3 < x < 5. \end{aligned}$$

We are here using dimensionless quantities, but some discussion of the relative magnitudes of these quantities are in order. The diffusion coefficient of polymer, $A_1 = \frac{f''(\phi_0)\phi_0^2(1-\phi_0)^2}{\kappa} = 0.0750$ is about 1/20 the size of the diffusion coefficients of the ions ($B_1 = 2$ and $B_2 = 4$) and is in the typically observed range [40]. The polymeric forces arising from $f(\phi)$ above are on the order of $c_{\text{water}}RT$ where c_{water} is the concentration of water. The concentration of ions is at most about 1/10 this concentration, and this is reflected in our magnitude of the ionic concentrations. The typical diffusion coefficient of ions is on the order of $10^{-5}\text{cm}^2/\text{sec}$. For a gel of size 1mm to $100\mu\text{m}$, this translates to a time scale of 10^3sec to 10sec . We also point out that, the Debye length is typically less than 1nm, thus justifying the electroneutral approximation if the gel size is on the order of 1mm to $100\mu\text{m}$

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, the variables c_k, ψ are changing rapidly near the interface, and a region of large spatial gradient forms for the concentrations. The graphs gradually flatten out and get close to the steady state solution. Figure 6.2 shows the location of $a(t)$ for $0 < t < 90$ while figure 6.3 shows the curve of $c_1(x, t)$ for $0 < x < a(t)$, $0 < t < 9$. The curve slowly converges to the uniform state as time gets larger and becomes uninteresting.

We track the changes of discrete L^2 norm ϕ, c_1 and ψ , and they all satisfy exponential decay to the equilibrium state. Some fittings of the computational re-

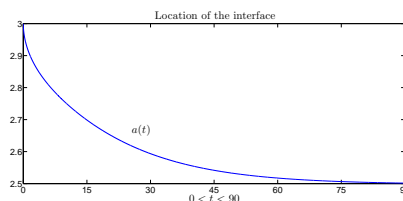


FIG. 6.2. Location of the interface

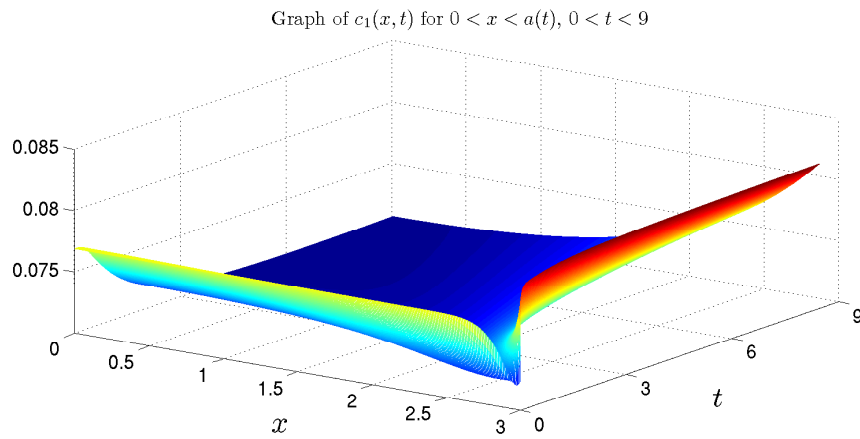


FIG. 6.3. Graph of $c_1(x, t)$
Exponential decay of ϕ

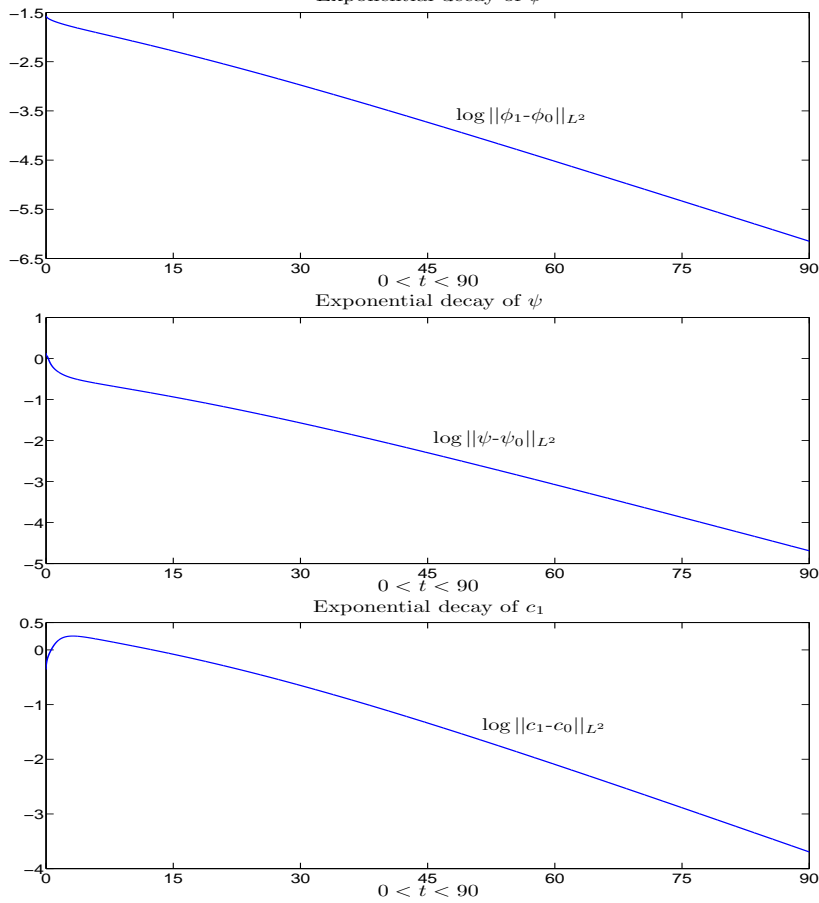


FIG. 6.4. Exponential decays in L^2

sults show that (we use $t = 150$)

$$\lambda_\phi \approx 0.0268, \lambda_\psi \approx 0.0265, \lambda_c \approx 0.0264 \quad (6.1)$$

which match the theoretical value $\lambda \approx 0.0269$ derived from (B.32).

7. Conclusion. In this paper, we briefly reviewed the model presented in the previous work [30] and applied Onsagers variational principle to rederive the dynamic equations and boundary conditions both in the mechanical case and in the ion electrodiffusive case. Under certain assumptions on the form of mechanical energy, especially convexity, we proved the uniqueness of steady state solution. We discussed the stability of the steady state in one spatial dimension, and obtained bounds on the decay rate. Finally, we developed a numerical scheme to simulate the polyelectrolyte gel model. The simulation showed us that the system undergoes a transient state at the beginning, and quickly approaches the equilibrium state with exponential decay. This validates the energy dissipation rule and the stability calculation.

As stated in the Introduction, our goal is to study the volume phase transition, and this paper represents a necessary step in this direction. As we saw in this paper, a convex mechanical energy density results in a unique and spatially uniform stable steady state. This indicates that a non-convex mechanical energy density is needed to model the volume phase transition. This is in line with the popular practice of using double-well type energies to study phase transition dynamics [4, 32]. Introduction of a non-convex mechanical energy density requires the simultaneous incorporation of an interfacial energy associated with phase boundaries. This will likely result in an equation of Cahn-Hilliard type coupled to the equations presented in this paper. We point out that a double-well structure may not be needed in the presence of ions; just a mechanical energy density that is non-convex. This is suggested by ongoing work of the author and coworkers on an ODE model of volume phase transitions based in part on [8]. One of our target applications of the volume phase transition is to drug delivery devices, a gel oscillator capable of periodic drug release [29, 8]. In such devices, external chemical energy input is needed to drive the oscillation. In this paper, we only treated the case in which the gel system was isolated. In the future, we shall build upon the results of this paper to derive and analyze such models, and to develop numerical schemes to study the volume phase transition and its practical applications.

Appendix A. Derivation of the model with nonzero dielectric constant.

We consider the system with ionic species, when the dielectric constant is not zero. The electrostatic potential ψ no longer satisfies the electroneutrality condition (3.5)-(3.6). Instead, it satisfies the Poisson equation

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

where ϵ is the dielectric constant which may depend on ϕ_1 in Ω_t . The above equation for ψ should be seen as giving ψ in terms of c_k 's, ϕ_1 and Ω_t .

The boundary conditions are given as follows. We still require (3.7)-(3.8) and (3.17). Moreover, on Γ_t , we assume the continuity of electrostatic potential and flux

$$[\psi] = [\epsilon \nabla \psi \cdot \mathbf{n}] = 0. \quad (A.2)$$

At the outer boundary $\partial\mathcal{U}$, we require no flux condition

$$\epsilon \nabla \psi \cdot \mathbf{n} = 0. \quad (A.3)$$

Now we define the potential energy \mathcal{U} by

$$\begin{aligned}\mathcal{U} &= U + E_{\text{ion}} + E_{\text{elec}} \\ &= U + \int_{\Omega_t} (\phi_2 \mathcal{W}_{\text{ion}}(c_k) + \mathcal{W}_{\text{elec}}) d\mathbf{x} + \int_{\mathcal{R}_t} (\mathcal{W}_{\text{ion}}(c_k) + \mathcal{W}_{\text{elec}})' d\mathbf{x},\end{aligned}\quad (\text{A.4})$$

in which (2.19)-(2.20), (3.10) are satisfied, and the electrostatic energy is defined by

$$\mathcal{W}_{\text{elec}} = \frac{1}{2} \epsilon |\nabla \psi|^2. \quad (\text{A.5})$$

Define the Rayleigh dissipation function by

$$\begin{aligned}\mathcal{W} &= W + \sum_{k=1}^N \int_{\Omega_t} \frac{1}{2} k_B T D_k^{-1} \phi_2^2 c_k |\mathbf{u}_k - \mathbf{v}_2|^2 d\mathbf{x} \\ &\quad + \sum_{k=1}^N \int_{\mathcal{R}_t} \frac{1}{2} k_B T D_k^{-1} c_k |\mathbf{u}_k - \mathbf{v}_f|^2 d\mathbf{x},\end{aligned}\quad (\text{A.6})$$

which is similar to (3.11).

We are ready to apply Onsager's variational principle to derive all of dynamic equations and boundary conditions. As before, we list them here for future reference. The stress tensors and body forces in (2.22) and (2.23) have to include the Maxwell stress tensor

$$\mathcal{T}_1 = \mathcal{T}_1^{\text{visc}} + \mathcal{T}_1^{\text{elas}} + \mathcal{T}_1^{\text{FH}} + \mathcal{T}_1^{\text{mw}}, \quad \mathcal{T}_{2,f} = \mathcal{T}_{2,f}^{\text{visc}}, \quad (\text{A.7})$$

$$\mathcal{T}_1^{\text{mw}} = \epsilon (\nabla \psi \otimes \nabla \psi - \frac{1}{2} |\nabla \psi|^2 I) + \frac{1}{2} \phi_1 \frac{\partial \epsilon}{\partial \phi_1} |\nabla \psi|^2 I, \quad (\text{A.8})$$

and Helmholtz force

$$\begin{aligned}\mathbf{f}_1 &= \mathbf{f}^{\text{fric}} + \mathbf{f}_1^{\text{elec}} + \mathbf{f}^{\text{hel}}, \quad \mathbf{f}^{\text{hel}} = \frac{1}{2} \phi_1 \nabla \left(\frac{\partial \epsilon}{\partial \phi_1} |\nabla \psi|^2 \right) \\ \mathbf{f}_2 &= -\mathbf{f}^{\text{fric}} + \mathbf{f}_2^{\text{elec}}, \quad \mathbf{f}_f = \mathbf{f}_f^{\text{elec}} = - \left(\sum_{k=1}^N q z_k c_k \right) \nabla \psi,\end{aligned}\quad (\text{A.9})$$

in which \mathbf{u}_k 's are defined by (3.13). For boundary condition, the force balance equation (2.27) has to include the Maxwell stress:

$$\mathcal{T}_f \mathbf{n} - \mathcal{T}_1 \mathbf{n} - \mathcal{T}_2 \mathbf{n} - [\mathcal{T}_1^{\text{mw}}] \mathbf{n} + [p] \mathbf{n} = 0 \quad (\text{A.10})$$

Now we apply Onsager's variational method to derive (2.22), (2.23), (3.13)-(3.15), (2.28), (2.29) and (A.7)-(A.10). Define the functional

$$R = \dot{\mathcal{U}} + \mathcal{W} \quad (\text{A.11})$$

R is a function of the velocities. We want to find a set $\{\mathbf{u}_1, \dots, \mathbf{u}_N, \mathbf{v}_{1,2,f}\}$ that minimizes R . The main steps are similar to the calculations of neutral case. We only present calculations that differ from the previous one. First, in order to calculate $\dot{\mathcal{U}}$ in Ω_t , we consider the electrostatic energy. Multiply (3.1) by $q z_k \psi$, integrate over Ω_t , and take sum from $k = 1$ to N ,

$$0 = \int_{\Omega_t} \sum_{k=1}^N \left(q z_k \psi \frac{\partial(\phi_2 c_k)}{\partial t} + q z_k \psi \nabla \cdot (\phi_2 c_k \mathbf{u}_k) \right) d\mathbf{x}$$

$$\begin{aligned}
&= \sum_{k=1}^N \frac{d}{dt} \int_{\Omega_t} qz_k \psi \phi_2 c_k d\mathbf{x} - \sum_{k=1}^N \int_{\Omega_t} \left(qz_k \frac{\partial \psi}{\partial t} \phi_2 c_k + \nabla \cdot (qz_k \psi \phi_2 c_k \mathbf{v}_1) \right) d\mathbf{x} \\
&+ \sum_{k=1}^N \int_{\Omega_t} qz_k \psi \nabla \cdot (\phi_2 c_k \mathbf{u}_k) d\mathbf{x} \\
&= \frac{d}{dt} \int_{\Omega_t} \sum_{k=1}^N (\phi_2 qz_k c_k) \psi d\mathbf{x} - \int_{\Omega_t} \sum_{k=1}^N (\phi_2 qz_k c_k) \frac{\partial \psi}{\partial t} d\mathbf{x} \\
&- \int_{\Omega_t} \sum_{k=1}^N (\phi_2 qz_k c_k \nabla \psi \cdot \mathbf{u}_k) d\mathbf{x} + \int_{\Gamma_t} \sum_{k=1}^N qz_k \psi \phi_2 c_k (\mathbf{u}_k - \mathbf{v}_1) \cdot \mathbf{n} dS \\
&=: S_1 - S_2 - \int_{\Omega_t} \sum_{k=1}^N qz_k \phi_2 c_k \nabla \psi \cdot \mathbf{u}_k d\mathbf{x} + \int_{\Gamma_t} \sum_{k=1}^N qz_k \psi \phi_2 c_k (\mathbf{u}_k - \mathbf{v}_1) \cdot \mathbf{n} dS
\end{aligned}$$

Integrating (A.1) by parts, we derive the following identities to replace S_1 and S_2 in the above:

$$\begin{aligned}
S_1 &= \frac{d}{dt} \int_{\Omega_t} (-\nabla \cdot (\epsilon \nabla \psi) - \phi_1 \rho_p) \psi d\mathbf{x} \\
&= \frac{d}{dt} \int_{\Omega_t} \epsilon |\nabla \psi|^2 d\mathbf{x} - \frac{d}{dt} \int_{\Gamma_t} \epsilon \psi \frac{\partial \psi}{\partial \mathbf{n}} dS - \frac{d}{dt} \int_{\Omega_t} \psi \phi_1 \rho_p d\mathbf{x}; \\
S_2 &= \int_{\Omega_t} \frac{\partial \psi}{\partial t} (-\nabla \cdot (\epsilon \nabla \psi) - \phi_1 \rho_p) d\mathbf{x} \\
&= \int_{\Omega_t} \epsilon \nabla \psi \nabla \frac{\partial \psi}{\partial t} d\mathbf{x} - \int_{\Gamma_t} \epsilon \frac{\partial \psi}{\partial t} \frac{\partial \psi}{\partial \mathbf{n}} dS - \int_{\Omega_t} \frac{\partial \psi}{\partial t} \phi_1 \rho_p d\mathbf{x}.
\end{aligned}$$

Recalling (3.21), it follows that

$$\begin{aligned}
&\frac{d}{dt} \int_{\Omega_t} \phi_2 \mathcal{W}_{\text{ion}} + \epsilon |\nabla \psi|^2 d\mathbf{x} \\
&= \int_{\Omega_t} \sum_{k=1}^N \left(\phi_2 c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot (\mathbf{u}_k - \mathbf{v}_2) + qz_k \phi_2 c_k \nabla \psi \cdot \mathbf{u}_k \right) + \epsilon \nabla \psi \nabla \frac{\partial \psi}{\partial t} d\mathbf{x} \\
&+ \frac{d}{dt} \int_{\Gamma_t} \epsilon \psi \frac{\partial \psi}{\partial \mathbf{n}} dS + \frac{d}{dt} \int_{\Omega_t} \psi \phi_1 \rho_p d\mathbf{x} - \int_{\Omega_t} \frac{\partial \psi}{\partial t} \phi_1 \rho_p d\mathbf{x} + \int_{\Gamma_t} -\epsilon \frac{\partial \psi}{\partial t} \frac{\partial \psi}{\partial \mathbf{n}} \\
&+ \mathcal{W}_{\text{ion}} \phi_2 (\mathbf{v}_1 - \mathbf{v}_2) \cdot \mathbf{n} + \sum_{k=1}^N \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \phi_2 c_k (\mathbf{v}_2 - \mathbf{u}_k) \cdot \mathbf{n} - qz_k \psi \phi_2 c_k (\mathbf{u}_k - \mathbf{v}_1) \cdot \mathbf{n} \right) dS.
\end{aligned} \tag{A.12}$$

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 (2.11)($i = 1$) and (3.12). Finally, we subtract the following identity from (A.12),

$$\frac{d}{dt} \int_{\Omega_t} \frac{1}{2} \epsilon |\nabla \psi|^2 d\mathbf{x} = \int_{\Omega_t} \frac{1}{2} \frac{\partial \epsilon}{\partial t} |\nabla \psi|^2 + \epsilon \nabla \psi \cdot \nabla \frac{\partial \psi}{\partial t} + \int_{\Gamma_t} \frac{1}{2} \epsilon |\nabla \psi|^2 (\mathbf{v}_1 \cdot \mathbf{n}) dS$$

$$\begin{aligned}
&= \int_{\Omega_t} \frac{1}{2} \nabla \left(\frac{\partial \epsilon}{\partial \phi_1} |\nabla \psi|^2 \right) \cdot (\phi_1 \mathbf{v}_1) + \epsilon \nabla \psi \cdot \nabla \frac{\partial \psi}{\partial t} d\mathbf{x} \\
&+ \int_{\Gamma_t} -\frac{1}{2} \frac{\partial \epsilon}{\partial \phi_1} |\nabla \psi|^2 (\phi_1 \mathbf{v}_1) \cdot \mathbf{n} + \frac{1}{2} \epsilon |\nabla \psi|^2 (\mathbf{v}_1 \cdot \mathbf{n}) dS,
\end{aligned}$$

to get

$$\begin{aligned}
&\frac{d}{dt} \int_{\Omega_t} \phi_2 \mathcal{W}_{\text{ion}} + \mathcal{W}_{\text{elec}} d\mathbf{x} \\
&= \int_{\Omega_t} \sum_{k=1}^N \left(\phi_2 c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot (\mathbf{u}_k - \mathbf{v}_2) + qz_k \phi_2 c_k \nabla \psi \cdot \mathbf{u}_k \right) - f^{\text{hel}} \cdot \mathbf{v}_1 - f_1^{\text{elec}} \cdot \mathbf{v}_1 d\mathbf{x} \\
&+ \int_{\Gamma_t} \mathcal{W}_{\text{ion}} \phi_2 (\mathbf{v}_1 - \mathbf{v}_2) \cdot \mathbf{n} + \sum_{k=1}^N \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \phi_2 c_k (\mathbf{v}_2 - \mathbf{u}_k) \cdot \mathbf{n} - qz_k \psi \phi_2 c_k (\mathbf{u}_k - \mathbf{v}_1) \cdot \mathbf{n} \right) \\
&+ \frac{1}{2} \frac{\partial \epsilon}{\partial \phi_1} |\nabla \psi|^2 (\phi_1 \mathbf{v}_1) \cdot \mathbf{n} - \epsilon \frac{\partial \psi}{\partial t} \frac{\partial \psi}{\partial \mathbf{n}} - \frac{1}{2} \epsilon |\nabla \psi|^2 (\mathbf{v}_1 \cdot \mathbf{n}) dS + \frac{d}{dt} \int_{\Gamma_t} \epsilon \psi \frac{\partial \psi}{\partial \mathbf{n}} dS
\end{aligned} \tag{A.13}$$

For \mathcal{R}_t , we can similarly derive

$$\begin{aligned}
&\frac{d}{dt} \int_{\mathcal{R}_t} \mathcal{W}_{\text{ion}} + \mathcal{W}_{\text{elec}} d\mathbf{x} \\
&= \int_{\mathcal{R}_t} \sum_{k=1}^N \left(c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot \mathbf{u}_k + qz_k c_k \nabla \psi \cdot \mathbf{u}_k \right) - k_B T \nabla c_k \cdot \mathbf{v}_f d\mathbf{x} \\
&+ \int_{\Gamma_t} -\mathcal{W}_{\text{ion}} (\mathbf{v}_1 \cdot \mathbf{n}) + \sum_{k=1}^N \left(c_k \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} (\mathbf{u}_k \cdot \mathbf{n}) + qz_k \psi c_k (\mathbf{u}_k - \mathbf{v}_1) \cdot \mathbf{n} \right) \tag{A.14} \\
&+ \epsilon \frac{\partial \psi}{\partial t} \frac{\partial \psi}{\partial \mathbf{n}} + \frac{1}{2} \epsilon |\nabla \psi|^2 (\mathbf{v}_1 \cdot \mathbf{n}) dS - \frac{d}{dt} \int_{\Gamma_t} \epsilon \psi \frac{\partial \psi}{\partial \mathbf{n}} dS \\
&+ \int_{\partial \mathcal{U}} \sum_{k=1}^N \left(-c_k \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} - qz_k \psi c_k \right) (\mathbf{u}_k \cdot \mathbf{n}) - \epsilon \frac{\partial \psi}{\partial t} \frac{\partial \psi}{\partial \mathbf{n}} dS - \frac{d}{dt} \int_{\partial \mathcal{U}} \epsilon \psi \frac{\partial \psi}{\partial \mathbf{n}} dS.
\end{aligned}$$

The integrals on the last line vanish, due to (3.8) and (A.3). Adding (A.13) and (A.14), we have

$$\begin{aligned}
&\frac{d}{dt} \int_{\Omega_t} \phi_2 \mathcal{W}_{\text{ion}} + \mathcal{W}_{\text{elec}} d\mathbf{x} + \frac{d}{dt} \int_{\mathcal{R}_t} \mathcal{W}_{\text{ion}} + \mathcal{W}_{\text{elec}} d\mathbf{x} \\
&= \int_{\Omega_t} \sum_{k=1}^N \left(\phi_2 c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot (\mathbf{u}_k - \mathbf{v}_2) + qz_k \phi_2 c_k \nabla \psi \cdot \mathbf{u}_k \right) - (f^{\text{hel}} + f_1^{\text{elec}}) \cdot \mathbf{v}_1 d\mathbf{x} \\
&+ \int_{\mathcal{R}_t} \sum_{k=1}^N \left(c_k \nabla \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \right) \cdot \mathbf{u}_k + qz_k c_k \nabla \psi \cdot \mathbf{u}_k - k_B T \nabla c_k \cdot \mathbf{v}_f \right) d\mathbf{x} \\
&+ \int_{\Gamma_t} \mathcal{W}_{\text{ion}} (-\phi_1 \mathbf{v}_1 - \phi_2 \mathbf{v}_2) \cdot \mathbf{n} + \sum_{k=1}^N \left(\frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \phi_2 c_k (\mathbf{v}_2 - \mathbf{u}_k^+) \cdot \mathbf{n} + c_k \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} (\mathbf{u}_k \cdot \mathbf{n}) \right) \\
&+ \sum_{k=1}^N (-qz_k \phi_2 c_k \psi (\mathbf{u}_k^+ - \mathbf{v}_1) \cdot \mathbf{n} + qz_k c_k \psi (\mathbf{u}_k^- - \mathbf{v}_1) \cdot \mathbf{n}) + \frac{1}{2} \frac{\partial \epsilon}{\partial \phi_1} |\nabla \psi|^2 (\phi_1 \mathbf{v}_1) \cdot \mathbf{n}
\end{aligned}$$

$$- \left[\epsilon \frac{\partial \psi}{\partial t} \frac{\partial \psi}{\partial \mathbf{n}} \right] - \left[\frac{1}{2} \epsilon |\nabla \psi|^2 (\mathbf{v}_1 \cdot \mathbf{n}) \right] dS + \frac{d}{dt} \int_{\Gamma_t} \left[\epsilon \psi \frac{\partial \psi}{\partial \mathbf{n}} \right] dS. \quad (\text{A.15})$$

Now we collect (A.4)-(A.11) and (A.15), apply (2.34) and (2.35), to derive \mathcal{R} :

$$\begin{aligned} \mathcal{R} &= \int_{\Omega_t} -(\nabla \cdot \mathcal{T}_1) \cdot \mathbf{v}_1 - (\nabla \cdot \mathcal{T}_2) \cdot \mathbf{v}_2 + \frac{1}{2} \kappa |\mathbf{v}_1 - \mathbf{v}_2|^2 + \sum_{k=1}^N \frac{1}{2} k_B T D_k^{-1} \phi_2^2 c_k |\mathbf{u}_k - \mathbf{v}_2|^2 \\ &\quad + (\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) \cdot \nabla p d\mathbf{x} \\ &\quad + \int_{\mathcal{R}_t} -(\nabla \cdot \mathcal{T}_f) \cdot \mathbf{v}_f + \sum_{k=1}^N \frac{1}{2} k_B T D_k^{-1} c_k |\mathbf{u}_k - \mathbf{v}_f|^2 + \mathbf{v}_f \cdot \nabla p d\mathbf{x} \\ &\quad + A \text{ in (2.35) + RHS of (A.15)}. \end{aligned}$$

Due to incompressibility, the last integrand term in \mathcal{R}_t can be replaced by a surface integral term:

$$\int_{\mathcal{R}_t} \sum_{k=1}^N -k_B T \nabla c_k \cdot \mathbf{v}_f d\mathbf{x} = - \int_{\Gamma_t} \sum_{k=1}^N k_B T c_k (\mathbf{v}_f \cdot \mathbf{n}) dS.$$

Now (2.22), (2.23) and (3.13) are derived. For the boundary terms, our goal is to obtain (2.28), (2.29) and (A.10). Since $\left[\epsilon \psi \frac{\partial \psi}{\partial \mathbf{n}} \right] = 0$ from (A.2), the very last integral in (A.15) vanishes. The remaining surface integral terms of (A.15) are:

$$\begin{aligned} &\mathcal{W}_{\text{ion}}(-\phi_1 \mathbf{v}_1 - \phi_2 \mathbf{v}_2) \cdot \mathbf{n} + \sum_{k=1}^N c_k \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} (\phi_2 \mathbf{v}_2 - \phi_2 \mathbf{u}_k^+ + \mathbf{u}_k^-) \cdot \mathbf{n} \\ &- \sum_{k=1}^N k_B T c_k (\mathbf{v}_f \cdot \mathbf{n}) - q z_k \phi_2 c_k \psi (\mathbf{u}_k^+ - \mathbf{v}_1) \cdot \mathbf{n} + q z_k c_k \psi (\mathbf{u}_k^- - \mathbf{v}_1) \cdot \mathbf{n} \\ &+ A \text{ in (2.35) + } \frac{1}{2} \frac{\partial \epsilon}{\partial \phi_1} |\nabla \psi|^2 (\phi_1 \mathbf{v}_1) \cdot \mathbf{n} - \left[\epsilon \frac{\partial \psi}{\partial t} \frac{\partial \psi}{\partial \mathbf{n}} \right] - \left[\frac{1}{2} \epsilon |\nabla \psi|^2 (\mathbf{v}_1 \cdot \mathbf{n}) \right], \end{aligned}$$

We use (2.16), (3.7), (A.2) and the continuity of \mathcal{W}_{ion} to eliminate terms on the first and second lines. Finally, we need to show

$$\frac{1}{2} \frac{\partial \epsilon}{\partial \phi_1} |\nabla \psi|^2 (\phi_1 \mathbf{v}_1) \cdot \mathbf{n} - \left[\epsilon \frac{\partial \psi}{\partial t} \frac{\partial \psi}{\partial \mathbf{n}} \right] - \left[\frac{1}{2} \epsilon |\nabla \psi|^2 (\mathbf{v}_1 \cdot \mathbf{n}) \right] = [(\mathcal{T}_1^{\text{mw}} \mathbf{n}) \cdot \mathbf{v}_1].$$

More precisely, we need

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

Note that the continuity of ψ across Γ_t (see (A.2)) implies that the jump on the right hand side must be 0 given that \mathbf{v}_1 coincides with the velocity of Γ_t . Consequently, all the boundary integral terms reduce to

$$A + [(\mathcal{T}_1^{\text{mw}} \mathbf{n}) \cdot \mathbf{v}_1]. \quad (\text{A.16})$$

Now, similar to the calculations in the mechanical case, it is easy to obtain the boundary conditions (2.28), (2.29) and (A.10). Thus, we have derived all the equations and boundary conditions.

Appendix B. Decay rate estimates.

We temporarily assume

$$H = 0, \quad (\text{B.1})$$

and rewrite the equations (5.54)-(5.57) here for convenience.

$$-\lambda u = A_1 u_{xx} + A_2 (\psi_1^+)_x, \quad (\text{B.2})$$

$$-\lambda d_k^+ = B_k (d_k^+)_{xx} + B_k (\psi_1^+)_{xx}, \quad k = 1, 2, \quad (\text{B.3})$$

$$C_1 d_1^+ + C_2 d_2^+ = -u_x := w, \quad (\text{B.4})$$

in which

$$A_1 = \frac{f''(\phi_0)\phi_0^2(1-\phi_0)^2}{\kappa}, \quad A_2 = -\frac{\rho_p\phi_0(1-\phi_0)}{\kappa}, \quad (\text{B.5})$$

$$B_k = \frac{D_k^+}{1-\phi_0}, \quad C_k = -\frac{z_k^2\zeta_k e_k^+(1-\phi_0)^2}{\phi_0\rho_p}, \quad (\text{B.6})$$

$$A_{1,2}, \quad B_{1,2}, \quad C_{1,2} > 0. \quad (\text{B.7})$$

Recall (5.20) and (5.21), let

$$\zeta = z_1\zeta_1 = -z_2\zeta_2. \quad (\text{B.8})$$

Consequently

$$C_1 = \frac{z_1 e_1^+(1-\phi_0)}{e_1^+ - e_2^+}, \quad C_2 = -\frac{z_2 e_2^+(1-\phi_0)}{e_1^+ - e_2^+}. \quad (\text{B.9})$$

B.1. Derivation of eigenvalues. To solve equations (5.53), let us first consider $(0, a)$. Differentiate (B.2) w.r.t. x , add (B.3)($k=1,2$) multiplied by C_k , and use (B.4) to get

$$(A_2 + B_1 C_1 + B_2 C_2)(\psi_1^+)_{xx} - A_1 w_{xx} + B_1 C_1 (d_1^+)_{xx} + B_2 C_2 (d_2^+)_{xx} = 0. \quad (\text{B.10})$$

Integrate and use the boundary condition (5.53a) to obtain

$$\begin{aligned} (\psi_1^+)_x &= \frac{A_1 w_x - B_1 C_1 (d_1^+)_x - B_2 C_2 (d_2^+)_x}{A_2 + B_1 C_1 + B_2 C_2} \\ &= \frac{(A_1 - B_1)C_1}{A_2 + B_1 C_1 + B_2 C_2} (d_1^+)_x + \frac{(A_1 - B_2)C_2}{A_2 + B_1 C_1 + B_2 C_2} (d_2^+)_x \end{aligned} \quad (\text{B.11})$$

where we used (B.4) to eliminate u . Now apply (B.11) to (B.2)-(B.4), to derive

$$-\lambda \begin{bmatrix} d_1^+ \\ d_2^+ \end{bmatrix} = \begin{bmatrix} p & q \\ r & s \end{bmatrix} \cdot \frac{d^2}{dx^2} \begin{bmatrix} d_1^+ \\ d_2^+ \end{bmatrix} \quad \text{or} \quad \frac{d^2}{dx^2} \begin{bmatrix} d_1^+ \\ d_2^+ \end{bmatrix} = \frac{\lambda}{ps - rq} \begin{bmatrix} -s & q \\ r & -p \end{bmatrix} \begin{bmatrix} d_1^+ \\ d_2^+ \end{bmatrix} \quad (\text{B.12})$$

in which

$$\begin{aligned} p &= \frac{B_1(A_2 + B_2 C_2 + A_1 C_1)}{A_2 + B_1 C_1 + B_2 C_2}, & q &= \frac{B_1(A_1 - B_2)C_2}{A_2 + B_1 C_1 + B_2 C_2}, \\ r &= \frac{B_2(A_1 - B_1)C_1}{A_2 + B_1 C_1 + B_2 C_2}, & s &= \frac{B_2(A_2 + B_1 C_1 + A_1 C_2)}{A_2 + B_1 C_1 + B_2 C_2}. \end{aligned} \quad (\text{B.13})$$

To solve (B.12), we must compute the eigenvalues of the last matrix in (B.12). We need the following lemmas.

LEMMA B.1. *The determinant $ps - rq > 0$.*

Proof. A direct computation yields

$$(ps - rq)(A_2 + B_1C_1 + B_2C_2)^2(B_1B_2)^{-1} = A_2^2 + A_2B_2C_2 + A_1A_2C_1 + A_2B_1C_1 + A_1B_1C_1^2 + A_1A_2C_2 + A_1B_2C_2^2 + A_1B_2C_1C_2 + A_1B_1C_1C_2 > 0 \quad (\text{B.14})$$

since every term is positive. \square

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

Proof. It suffices to prove

$$\Delta' = (B_1A_2 + B_1B_2C_2 + B_1A_1C_1 - B_2A_2 - B_2B_1C_1 - B_2A_1C_2)^2 + 4B_1B_2C_1C_2(B_1 - A_1)(B_2 - A_1) \geq 0. \quad (\text{B.15})$$

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

$$\frac{\partial \Delta'}{\partial A_2} = 2(B_1 - B_2)(B_1A_2 - B_2A_2 + B_1B_2C_2 + B_1A_1C_1 - B_2B_1C_1 - B_2A_1C_2), \quad (\text{B.16})$$

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

$$A_2 = \frac{(A_1 - B_1)B_2C_2 + (B_2 - A_1)B_1C_1}{B_1 - B_2} < 0 \quad (\text{B.17})$$

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

$$\Delta'(A_2 = 0) = (B_1C_1(B_2 - A_1) + B_2C_2(B_1 - A_1))^2 > 0, \quad (\text{B.18})$$

$$\Delta'(A_2 = \infty) = (B_1 - B_2)^2 \cdot \infty = \infty, \quad (\text{B.19})$$

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

From the above lemma, $\Delta = 0$ if and only if $A_1 = B_1 = B_2$, for which the matrix becomes multiple of the identity matrix. The eigenvalues of (B.12) can be expressed by $\omega_1^2\lambda, \omega_2^2\lambda$, and $\omega_1 \geq \omega_2 > 0$ satisfy

$$(ps - rq)\omega^4 - (p + s)\omega^2 + 1 = 0. \quad (\text{B.20})$$

They are given by

$$\omega_1^2 := \frac{p + s + \sqrt{(p - s)^2 + 4rq}}{2(ps - rq)}, \quad \omega_2^2 := \frac{p + s - \sqrt{(p - s)^2 + 4rq}}{2(ps - rq)} \quad (\text{B.21})$$

We consider the generic situation that $A_1 \neq B_1, B_2$. From (B.12) we have

$$rq \neq 0. \quad (\text{B.22})$$

The equal case is much simpler and will be mentioned later when necessary. From the boundary conditions (5.53a) and (B.11), $(d_k^+)_x = 0$ at $x = 0$. Therefore, d_1^+ and d_2^+ are linear combinations of $\cos(\omega_1\sqrt{\lambda}x)$ and $\cos(\omega_2\sqrt{\lambda}x)$, and

$$\begin{bmatrix} d_1^+ \\ d_2^+ \end{bmatrix} = \begin{bmatrix} 1 - s\omega_1^2 \\ r\omega_1^2 \end{bmatrix} \alpha \cos(\omega_1\sqrt{\lambda}x) + \begin{bmatrix} q\omega_2^2 \\ 1 - p\omega_2^2 \end{bmatrix} \beta \cos(\omega_2\sqrt{\lambda}x). \quad (\text{B.23})$$

Let us now consider (a, L) , equations (5.53h)-(5.53j). Without loss of generality, let $\psi_0^- = 0$ and we have

$$e_1^- = e_2^- = 1. \quad (\text{B.24})$$

A similar calculation in (a, L) reveals

$$(\psi_1^-)_{xx} = \frac{z_1(D_2^- - D_1^-)}{z_1 D_1^- - z_2 D_2^-} (d_1^-)_{xx}, \quad d_2^- = \frac{z_1}{z_2} d_1^-. \quad (\text{B.25})$$

Apply (B.25) to (5.53j) to derive $(d_1^-)_x = 0$ at $x = L$. Therefore, we may let

$$d_1^- = \gamma \cos(\omega \sqrt{\lambda}(x - L)), \quad \omega = \sqrt{\frac{(z_1 D_1^- - z_2 D_2^-)}{(z_1 - z_2) D_1^- D_2^-}}. \quad (\text{B.26})$$

We now turn to boundary conditions at $x = a$, (5.53e)-(5.53g). Use (B.2) to get

$$\begin{aligned} \lambda u &= A_1 w_x - A_2 (\psi_1^+)_x \\ &= \frac{A_1 B_1 C_1 + A_1 B_2 C_2 + A_2 B_1}{A_2 + B_1 C_1 + B_2 C_2} C_1 (d_1^+)_x + \frac{A_1 B_1 C_1 + A_1 B_2 C_2 + A_2 B_2}{A_2 + B_1 C_1 + B_2 C_2} C_2 (d_2^+)_x. \end{aligned} \quad (\text{B.27})$$

From (B.11), it follows that (5.53e) with $k = 1$ becomes

$$\begin{aligned} &\left(\left(A_1 C_1 - \frac{A_2 r}{B_2} \right) (d_1^+)_x + \left(A_1 C_2 - \frac{A_2 q}{B_1} \right) (d_2^+)_x \right) (e_1^+ - 1) \\ &= z_1 \left(D_1^+ e_1^+ \left(1 + \frac{r}{B_2} \right) (d_1^+)_x + D_1^+ e_1^+ \left(\frac{q}{B_1} \right) (d_2^+)_x - \omega^{-2} (d_1^-)_x \right). \end{aligned} \quad (\text{B.28})$$

Equation (5.53e) with $k = 2$ is equivalent to (B.28), as it is (B.28) multiplied by z_2/z_1 . Eliminate ψ_1 from (5.53f), to get

$$[d_1] = [d_2] \iff d_1^+ - d_2^+ = -\frac{z_1 - z_2}{z_2} d_1^-. \quad (\text{B.29})$$

Finally, (5.53g) becomes

$$(e_1^+ + \phi_0^2 f''(\phi_0) C_1 \zeta^{-1}) d_1^+ + (-e_2^+ + \phi_0^2 f''(\phi_0) C_2 \zeta^{-1}) d_2^+ = -\frac{z_1 - z_2}{z_2} d_1^-, \quad (\text{B.30})$$

where (B.8) is used. (B.29) and (B.30) cannot be equivalent, since

$$\begin{aligned} &\zeta e_1^+ + \phi_0^2 f''(\phi_0) C_1 - \zeta e_2^+ + \phi_0^2 f''(\phi_0) C_2 \\ &= \phi_0^2 f''(\phi_0) (C_1 + C_2) + \zeta (e_1^+ - e_2^+) > 0, \end{aligned} \quad (\text{B.31})$$

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

Now the system (5.53a)-(5.53j) is reduced to (B.28)-(B.30) in which $\{d_1^+, d_2^+, d_1^-\}$ are defined by (B.23) and (B.26). There are four unknowns $\{\alpha, \beta, \gamma, \lambda\}$, but $\lambda^* > 0$

is an eigenvalue only if the linear system for $\{\alpha, \beta, \gamma\}$ has nontrivial solutions when $\lambda = \lambda^*$. We rewrite (B.28)-(B.30) in the matrix form: $\mathcal{A}[\alpha \ \beta \ \gamma]^T =$

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

in which

$$a_{11} = 1 - (s + r)\omega_1^2, \quad a_{12} = (p + q)\omega_2^2 - 1, \quad (\text{B.33})$$

$$a_{21} = (e_1^+ + \phi_0^2 f''(\phi_0) C_1 \zeta^{-1})(1 - s\omega_1^2) + (-e_2^+ + \phi_0^2 f''(\phi_0) C_2 \zeta^{-1})(r\omega_1^2), \quad (\text{B.34})$$

$$a_{22} = (e_1^+ + \phi_0^2 f''(\phi_0) C_1 \zeta^{-1})(q\omega_2^2) + (-e_2^+ + \phi_0^2 f''(\phi_0) C_2 \zeta^{-1})(1 - p\omega_2^2). \quad (\text{B.35})$$

To find a convenient expression for a_{31} and a_{32} , we rewrite (B.28) as follows.

$$M_1(d_1^+)_x + M_2(d_2^+)_x + z_1 \omega^{-2} (d_1^-)_x = 0, \quad (\text{B.36})$$

$$\begin{aligned} M_1 &= \frac{A_1 B_1 C_1 + A_1 B_2 C_2 + A_2 B_1}{A_2 + B_1 C_1 + B_2 C_2} \cdot C_1 (e_1^+ - 1) - \frac{A_2 + B_2 C_2 + A_1 C_1}{A_2 + B_1 C_1 + B_2 C_2} \cdot z_1 D_1^+ e_1^+ \\ &= (pC_1 + rC_2)(e_1^+ - 1) - (pB_1^{-1}) \cdot z_1 D_1^+ e_1^+ \\ &= (1 - \phi_0) \left(-z_1 e_1^+ p \cdot \frac{1 - e_2^+}{e_1^+ - e_2^+} - z_2 e_2^+ r \cdot \frac{e_1^+ - 1}{e_1^+ - e_2^+} \right) \\ &= (1 - \phi_0) (-z_1 e_1^+ p \tau - z_2 e_2^+ r (1 - \tau)), \quad \tau = \frac{1 - e_2^+}{e_1^+ - e_2^+} \in (0, 1), \end{aligned} \quad (\text{B.37})$$

$$\begin{aligned} M_2 &= \frac{A_1 B_1 C_1 + A_1 B_2 C_2 + A_2 B_2}{A_2 + B_1 C_1 + B_2 C_2} \cdot C_2 (e_1^+ - 1) - \frac{(A_1 - B_2) C_2}{A_2 + B_1 C_1 + B_2 C_2} \cdot z_1 D_1^+ e_1^+ \\ &= (sC_2 + qC_1)(e_1^+ - 1) - (qB_1^{-1}) \cdot z_1 D_1^+ e_1^+ \\ &= (1 - \phi_0) \left(-z_1 e_1^+ q \cdot \frac{1 - e_2^+}{e_1^+ - e_2^+} - z_2 e_2^+ s \cdot \frac{e_1^+ - 1}{e_1^+ - e_2^+} \right) \\ &= (1 - \phi_0) (-z_1 e_1^+ q \tau - z_2 e_2^+ s (1 - \tau)). \end{aligned} \quad (\text{B.38})$$

The above calculation implies

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

B.2. Upper and lower bound estimates. We have derived and simplified the matrix \mathcal{A} from which the eigenvalues λ 's are implicitly determined, namely $\det(\mathcal{A}(\lambda)) = 0$. In this section, we seek upper and lower bounds for the principal eigenvalue λ_1 , and it turns out that they are closely related to PEP and PEIs defined in section 5.2. Given the expression of $\det(\mathcal{A}(\lambda))$ in (B.32), the estimate is difficult in general; however, it is possible if we assume

$$A_1 < B_1, B_2. \quad (\text{B.39})$$

This is a reasonable assumption, given remark 5.4.

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 $\tan(\omega\sqrt{\lambda}(L-a))$. Since 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

$$\max\{\omega_1\sqrt{\lambda_1}a, \omega\sqrt{\lambda_1}(L-a)\} < \frac{3\pi}{2} \quad \text{or} \quad \lambda < \frac{3\pi}{2} \cdot \min\{(a\omega_1)^{-2}, ((L-a)\omega)^{-2}\}. \quad (\text{B.40})$$

We need to estimate ω_1 . Consider a quantity u that satisfies

$$u^2 - (p+s)u + (ps-rq) \leq 0. \quad (\text{B.41})$$

From (B.20) it is clear that

$$\omega_1^2 \geq \frac{1}{u} \geq \omega_2^2. \quad (\text{B.42})$$

Since $r, q < 0$ from (B.39), $u = p, s$ satisfy (B.41), therefore

$$\omega_1^2 \geq \frac{1}{p}, \quad \frac{1}{s} \geq \omega_2^2. \quad (\text{B.43})$$

Again, from (B.39), $p < B_1$, $s < B_2$, we have

$$\lambda_1 < \left(\frac{3\pi}{2}\right)^2 \cdot \min\left\{\frac{B_1}{a^2}, \frac{B_2}{a^2}, \frac{(z_1 - z_2)D_1^- D_2^-}{(L-a)^2(z_1 D_1^- - z_2 D_2^-)}\right\}. \quad (\text{B.44})$$

This estimate is also valid when any of the cosine function vanishes.

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, provided $D_1 \leq D_2$.

We turn to the 3-by-3 matrix in (B.32). 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

$$\chi = \frac{e_1^+ - 1 + \phi_0^2 f''(\phi_0)C_1\zeta^{-1}}{e_1^+ - e_2^+ + \phi_0^2 f''(\phi_0)(C_1 + C_2)\zeta^{-1}}, \quad \chi \in (0, 1), \quad (\text{B.45})$$

the matrix can be written as $M =$

$$\begin{bmatrix} 1 - (s+r)\omega_1^2 & (p+q)\omega_2^2 - 1 & \frac{z_1 - z_2}{z_2} \\ \chi(1 - s\omega_1^2) + (1 - \chi)(r\omega_1^2) & \chi(q\omega_2^2) + (1 - \chi)(1 - p\omega_2^2) & 0 \\ a_{31}\omega_1 \tan(\omega_1\sqrt{\lambda}a) & a_{32}\omega_2 \tan(\omega_2\sqrt{\lambda}a) & \frac{z_1}{\omega} \tan(\omega\sqrt{\lambda}(L-a)) \end{bmatrix}, \quad (\text{B.46})$$

$$a_{31} = (1 - \phi_0)(z_1 e_1^+ \tau(p - (ps - rq)\omega_1^2) + z_2 e_2^+ (1 - \tau)r), \quad (\text{B.47})$$

$$a_{32} = (1 - \phi_0)(z_1 e_1^+ \tau q + z_2 e_2^+ (1 - \tau)(s - (ps - rq)\omega_2^2)). \quad (\text{B.48})$$

and we denote

$$\det(M) = K_1 \tan(\omega_1 \sqrt{\lambda} a) + K_2 \tan(\omega_2 \sqrt{\lambda} a) + K_3 \tan(\omega \sqrt{\lambda} (L - a)). \quad (\text{B.49})$$

Now we claim that K_1, K_2, K_3 are all negative. Since the calculation is very long, we divide it into several steps: (1) $K_2, K_3 < 0$; (2) let $D_1 \leq D_2$, then $K_1 < 0$ in the case $z_1 = -z_2$; (3) $K_1 < 0$ for any $z_1 > 0 > z_2$.

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 (B.41)-(B.43) it follows that $M_{21} < 0$, and

$$s - (ps - rq)\omega_2^2 = \frac{(s - p) + \sqrt{(s - p)^2 + 4rq}}{2} > 0, \quad (\text{B.50})$$

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

$$M_{11}M_{22} - M_{21}M_{12} = (1 - s\omega_1^2)(1 - p\omega_2^2) - rq\omega_1^2\omega_2^2 < 0, \quad (\text{B.51})$$

we obtain $K_3 < 0$.

Proof of (2). We consider a special case when $z_1 = -z_2 = z > 0$. For convenience let

$$\begin{aligned} x = e_1^+ > 1, \quad A_2 &= (1 - \phi_0) \cdot \frac{z}{x - \frac{1}{x}} \cdot A'_2, \\ p &= \frac{B_1(A_1x + A'_2 + B_2/x)}{B_1x + A'_2 + B_2/x}, \quad q = -\frac{B_1(B_2 - A_1)/x}{B_1x + A'_2 + B_2/x}, \\ r &= -\frac{B_2(B_1 - A_1)x}{B_1x + A'_2 + B_2/x}, \quad s = \frac{B_2(B_1x + A'_2 + A_1/x)}{B_1x + A'_2 + B_2/x}. \end{aligned} \quad (\text{B.52})$$

Apply (B.52) to the numerator of χ in (B.45),

$$\begin{aligned} &x - 1 + \phi_0^2(1 - \phi_0)f''(\phi_0)z\zeta^{-1} \cdot \frac{x}{x - \frac{1}{x}} \\ &< x^2 \cdot \left(1 - \frac{1}{x} + \phi_0^2(1 - \phi_0)f''(\phi_0)z\zeta^{-1} \cdot \frac{\frac{1}{x}}{x - \frac{1}{x}}\right) \\ &\Rightarrow \chi < x^2(1 - \chi), \end{aligned} \quad (\text{B.53})$$

and then

$$\begin{aligned} M_{22} &= \chi(q\omega_2^2) + (1 - \chi)(1 - p\omega_2^2) \\ &> (1 - \chi)(x^2q\omega_2^2 + 1 - p\omega_2^2) = (1 - \chi)(1 - (p - x^2q)\omega_2^2). \end{aligned} \quad (\text{B.54})$$

Let $u = p - x^2q$ in (B.41)-(B.43). With some calculation,

$$u^2 - u(p + s) + ps - rq = -q(x^2p - x^4q - x^2s + r) = -q \cdot \frac{(B_1 - B_2)A'_2x^2}{B_1x + A'_2 + B_2/x} < 0, \quad (\text{B.55})$$

which indicates $M_{22} > 0$ in (B.54). Notice that we use the assumption (5.62) or equivalently $B_1 \leq B_2$ here.

We now show $a_{31} < 0$. First, we have

$$s - p = \frac{B_1(B_2 - A_1)x + (B_2 - B_1)A'_2 + B_2(A_1 - B_1)/x}{B_1x + A'_2 + B_2/x}. \quad (\text{B.56})$$

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

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

Since $a_{31} < 0$ and $M_{22} > 0$, we have $K_1 < 0$.

Proof of (3). We turn to the more general case when $z_2 = -hz_1$, $e_2^+ = x^{-h}$. Define A_2' in a similar manner and the main approach is similar to (2). It can be seen that (B.53) becomes $\chi < h^{-1}x^{1+h}(1 - \chi)$. Use $u = p - h^{-1}x^{1+h}q$ in (B.55) to derive $M_{22} > 0$. Here we must require (5.62).

To show $a_{31} < 0$, we need $a_{31} =$

$$\begin{aligned} (1 - \phi_0) \cdot \frac{z}{x - x^{-h}} \left(-(x - x^{1-h}) \cdot \frac{s - p + \sqrt{(s-p)^2 + 4rq}}{2} - h(x-1)x^{-h}r \right) < 0 \\ \text{or } \frac{s - p + \sqrt{(s-p)^2 + 4rq}}{2} > \frac{h(x-1)x^{-h}}{x - x^{1-h}} \cdot (-r). \end{aligned}$$

It will suffice if

$$s - p > \frac{h(x-1)x^{-h}}{x - x^{1-h}} \cdot (-r) - \frac{x - x^{1-h}}{h(x-1)x^{-h}} \cdot (-q).$$

Span all the terms and calculate directly, and use the fact that

$$\begin{aligned} B_1(B_2 - A_1) &> B_2(B_1 - A_1); \\ x + \frac{x - x^{1-h}}{x - 1} &= \frac{x^2 - x^{1-h}}{x - 1} > \frac{(x^2 - x^{1-h})hx^{-h}}{x - x^{1-h}} = hx^{-h} + \frac{h(x-1)x^{1-h}}{x - x^{1-h}}. \end{aligned}$$

It follows that $a_{31} < 0$.

Now we have shown $K_{1,2,3} < 0$ in (B.49), and thus

$$\lambda_1 \geq \frac{\pi^2}{4} \cdot \min \left\{ \frac{1}{\omega_1^2 a^2}, \frac{1}{\omega^2 (L-a)^2} \right\}. \quad (\text{B.57})$$

The equality occurs when some cosine functions in (B.32) take zero value. Furthermore,

$$\begin{aligned} (p - A_1)(s - A_1) &= \frac{(B_1 - A_1)(B_2 - A_1)(A_2 + B_1 C_1)(A_2 + B_2 C_2)}{(A_2 + B_1 C_1 + B_2 C_2)^2} \\ &> \frac{(B_1 - A_1)(B_2 - A_1)B_1 B_2 C_1 C_2}{(A_2 + B_1 C_1 + B_2 C_2)^2} = rq, \\ \Rightarrow ps - rq &> A_1(p + s - A_1) > A_1 \cdot \frac{p + s}{2} \quad \text{or} \quad \frac{ps - rq}{A_1} - \frac{p + s}{2} > 0, \\ \Rightarrow \omega_1^2 &= \frac{p + s + \sqrt{(p-s)^2 + 4rq}}{2(ps - rq)} < \frac{1}{A_1}. \end{aligned}$$

Therefore, from (B.57) we derive

$$\lambda_1 \geq \frac{\pi^2}{4} \cdot \min \left\{ \frac{A_1}{a^2}, \frac{(z_1 - z_2)D_1^- D_2^-}{(z_1 D_1^- - z_2 D_2^-)(L - a)^2} \right\}. \quad (\text{B.58})$$

In the above calculation, it is assumed $H = 0$ in (B.1). Actually, this condition is not necessary, since H only appears in A_1 and we only used the property $A_1 > 0$ in the above calculation. Now assume $H \neq 0$, there are two possibilities. If

$$A_1 = \frac{(1 - \phi_0)^2(-\lambda H + \phi_0^2 f''(\phi_0))}{\kappa} > 0, \quad (\text{B.59})$$

(B.58) remains valid, and A_1 is replaced by (B.59), we have

$$\lambda \geq \min \left\{ \frac{\phi_0^2 f''(\phi_0)}{\frac{4a^2 \kappa}{\pi^2(1-\phi_0)^2} + H}, \frac{\pi^2}{4(L-a)^2} \cdot \frac{(z_1 - z_2)D_1^- D_2^-}{(z_1 D_1^- - z_2 D_2^-)} \right\}, \quad (\text{B.60})$$

and upper bound estimate (B.44). If (B.59) is not true, then

$$A_1 = \frac{(1 - \phi_0)^2(-\lambda H + \phi_0^2 f''(\phi_0))}{\kappa} < 0, \text{ hence } \lambda > \frac{\phi_0^2 f''(\phi_0)}{H}. \quad (\text{B.61})$$

This inequality is stronger than (B.60), therefore we still get (B.60).

Now we have proved Theorem 5.3 when the inequality in (5.60) is strict. If the equality holds, (B.23) is still valid thanks to $p < s$. The computation thereafter is the same or simpler.

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