

# A DYNAMIC MODEL OF POLYELECTROLYTE GELS

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**Abstract.** We derive a model of the coupled mechanical and electrochemical effects of polyelectrolyte gels. We assume that the gel, which is immersed in a fluid domain, is an immiscible and incompressible mixture of a solid polymeric component and the fluid. As the gel swells and de-swells, the gel-fluid interface can move. Our model consists of a system of partial differential equations for mass and linear momentum balance of the polymer and fluid components of the gel, the Navier-Stokes equations in the surrounding fluid domain, and the Poisson-Nernst-Planck equations for the ionic concentrations on the whole domain. These are supplemented by a novel and general class of boundary conditions expressing mass and linear momentum balance across the moving gel-fluid interface. Our boundary conditions include the permeability boundary conditions proposed in earlier studies. A salient feature of our model is that it satisfies a free energy dissipation identity, in accordance with the second law of thermodynamics. We also show, using boundary layer analysis, that the well-established Donnan condition for equilibrium arises naturally as a consequence of taking the electroneutral limit in our model.

**1. Introduction.** Gels are crosslinked, three dimensional polymer networks that absorb solvent and swell without dissolution [25, 26, 17, 44, 4]. Some gels can experience large changes in volume in response to small changes in various environmental parameters including temperature, pH or the ionic composition of the solvent [42]. In some gels, this change is discontinuous with respect to changes in the environmental parameter. This is the volume phase transition, first described in [43]. One interesting feature of the volume phase transition is that it exhibits hysteresis, a feature that distinguishes it from the familiar liquid-gas phase transition [42, 13]. These large volume changes have found use in various artificial devices including disposable diapers [37], drug delivery devices [35, 10] and chemical actuators [14, 22]. Gels abound in nature are thought to play an important role in certain physiological systems [53, 47]. The study of gel swelling, and more generally of gel dynamics, is thus important from both practical and theoretical standpoints.

In this paper, we focus on polyelectrolyte gels; the polymer network contains fixed charge groups that dissociate and deliver counterions into the solvent. Polyelectrolyte gels form an important class of gels studied experimentally and used in applications. Indeed, the volume phase transition is most easily realized in polyelectrolyte gels [15, 42]. Most biological gels are also of this type.

Many of the early theoretical studies on gels focused on the static equilibrium state. A pioneering study on the dynamics of gels is [45], in which the authors examine the dynamics of an electrically neutral gel around an equilibrium swelled state. As such, this was a small deformation theory. The dynamic theory of electrically neutral gels has since been developed by many authors [8, 51, 39, 11, 12, 28, 29].

Statics of polyelectrolyte gels are studied in [38], which has since been extended in many directions [42, 23]. The dynamics of polyelectrolyte gels has also received a great deal of attention, and systems of evolution equations have been proposed by many authors [18, 16, 19, 31, 34, 49, 48, 52, 32, 9, 1, 23]. A standard approach, which we adopt in this paper, is to treat polyelectrolyte gels as a two phase medium of polymer network and fluid, with the ions being treated as solute species dissolved in the fluid. But even within this same approach, there are various disagreements among the different models proposed by different authors.

In this paper, we propose a system of partial differential equations (PDEs) describing the dynamics of a polyelectrolyte gel immersed in fluid. The distinguishing feature of our model is that its formulation is guided by the requirement that the

system, as a whole, must satisfy a free energy identity. This energetic framework allows for the unambiguous determination of the form of the ionic electrodiffusion equations and of the coupling between electrical effects and the mechanics of the gel. This clarifies the confusion seen among different models proposed in the literature on the dynamics of polyelectrolyte gels. The energetic approach also allows for the formulation of general interface conditions at the gel-fluid interface; indeed, in previous work, the treatment of boundary or interface conditions has been simplistic, if not an afterthought. We also examine the electroneutral limit. In this limit, we recover the Donnan equilibrium condition at the gel-fluid interface.

The paper is organized as follows. In Section 2, we present the skeletal framework of our model. The gel is treated as a two-phase medium consisting of the polymer network phase and a fluid phase. We write down general mass and momentum balance equations as well as the interface conditions at the gel-fluid interface.

In Section 3, we propose a purely mechanical model of a neutral gel immersed in fluid. We specify the polymer stress and fluid stresses and the body force acting between the polymer network and fluid. We propose a novel class of boundary conditions at the gel-fluid interface. Some previously proposed boundary conditions can be seen as limiting cases of the general class we present here [8, 51, 39]. We then prove a free energy identity satisfied by this system.

In Section 4, we discuss the inclusion of ionic electrodiffusion. The ions satisfy the electrodiffusion-advection equations and the electrostatic potential satisfies the Poisson equation. The mechanical stress and body forces set forth in Section 3 are now augmented by the electrical forces. We conclude the section by showing that this system too satisfies a free energy identity.

The Debye length is often very small in polyelectrolyte gels, and thus the gel as well as the surrounding fluid is nearly electroneutral except for thin boundary layers that may form at the gel-fluid interface. For gels at physiological salt concentrations, for example, the Debye length is on the order of 1nm [40]. In Section 5, we formulate the appropriate equations in this electroneutral limit. We perform a boundary layer analysis to deduce the appropriate interface conditions in the electroneutral limit and find that the van't Hoff law for osmotic pressure arises naturally in this limit. It is easily checked that the condition for steady state gives us the well-established Donnan condition, set forth in the context of polyelectrolyte gels in [38].

**2. Mass, Momentum and Energy Balance.** We consider a gel that is in contact with its own fluid. We model the gel as an immiscible, incompressible mixture of two components, polymer network and solvent. The gel and the fluid occupy a smooth bounded region  $\mathbb{U} \subset \mathbb{R}^3$ . Let  $\Omega_t \subset \mathbb{U}$  be the region where the gel is present at time  $t$ . We assume that  $\Gamma_t \equiv \partial\Omega_t, \Gamma_t \cap \partial\mathbb{U} = \emptyset$ . This means that the gel is completely immersed in the fluid. We denote the fluid region by  $\mathcal{R}_t \equiv \mathbb{U} \setminus (\Omega_t \cup \Gamma_t)$  (Figure 2.1).

At each point in  $\Omega_t$ , define the volume fractions of the polymer component  $\phi_1$  and that of the solvent component  $\phi_2$ . Assuming that there are neither voids nor additional volume-occupying components in the system, we have:

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

for any point inside  $\Omega_t$ . Let  $\mathbf{v}_i, i = 1, 2$  be the velocities of the polymer and solvent components respectively. The volume fractions  $\phi_1$  and  $\phi_2$  satisfy the volume transport equations:

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

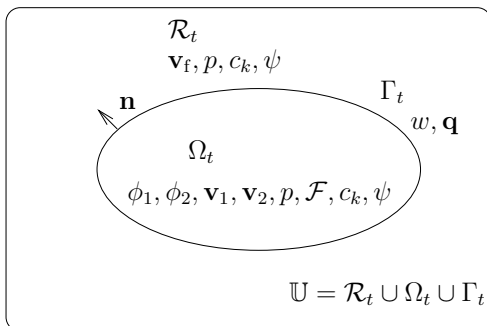


FIG. 2.1. A schematic of a gel immersed in fluid. The regions  $\Omega_t$  and  $\mathcal{R}_t$  are the gel and fluid regions respectively and  $\Gamma_t$  is the gel-fluid interface. The dependent variables in  $\Omega_t$  are:  $\phi_1, \phi_2, \mathbf{v}_1, \mathbf{v}_2, p, \mathcal{F}, c_k (k = 1, \dots, N), \psi$ . In  $\mathcal{R}_t$ , they are:  $\mathbf{v}_f, p, c_k (k = 1, \dots, N), \psi$ .  $\mathcal{F}$  is the deformation gradient, to be discussed in Section 3.  $c_k$  are the ionic concentrations and  $\psi$  is the electrostatic potential, discussed in Section 4. At the gel-fluid interface  $\Gamma_t$ , we have the variables  $w$  and  $\mathbf{q}$  defined in (2.13) and (2.14) respectively.

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

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

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

Force balance is given as follows:

$$0 = \nabla \cdot \mathcal{T}_i - \phi_i \nabla p_i + \mathbf{f}_i + \mathbf{g}_i, \quad i = 1, 2 \quad (2.4)$$

where  $\mathcal{T}_i$  and  $p_i$  are the stress tensors and pressures in the polymer and solvent components. The term  $\mathbf{f}_i + \mathbf{g}_i$  is the body force, which we divide into two parts for reasons that will become clear below. Inertial effects are seldom, if ever, significant in gel dynamics, and we have thus neglected inertial terms. We henceforth let:

$$p_1 = p + p_\Delta, \quad p_2 = p. \quad (2.5)$$

We shall refer to  $p_2 = p$  as the pressure and to  $p_\Delta$  as the pressure difference. This pressure difference is referred to as the capillary pressure in the theory of mixtures [7, 46]. The pressure  $p$  is determined by the incompressibility constraint. We require that  $p_\Delta$  and  $\mathbf{f}_i$  satisfy the following condition. There exists a tensor  $\mathcal{S}_g$  such that:

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

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

$$0 = \nabla \cdot (\mathcal{T}_1 + \mathcal{T}_2 + \mathcal{S}_g - pI) + \mathbf{g}_1 + \mathbf{g}_2, \quad (2.7)$$

where  $I$  is the  $3 \times 3$  identity matrix. Condition (2.6) thus ensures that the total force acting on the gel at each point can be written as the divergence of a tensor except for the body forces  $\mathbf{g}_i$ . To ensure local force balance, we require

$$\mathbf{g}_1 + \mathbf{g}_2 = 0. \quad (2.8)$$

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

$$0 = \nabla \cdot \mathcal{T}_f - \nabla p + \mathbf{f}_f, \quad (2.9)$$

$$\nabla \cdot \mathbf{v}_f = 0, \quad (2.10)$$

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

$$\nabla \cdot \mathcal{S}_f = \mathbf{f}_f. \quad (2.11)$$

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

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

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

$$\mathbf{v}_1 \cdot \mathbf{n} = v_\Gamma \text{ on } \Gamma_t. \quad (2.12)$$

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

$$(\mathbf{v}_f - \mathbf{v}_1) \cdot \mathbf{n} = \phi_2(\mathbf{v}_2 - \mathbf{v}_1) \cdot \mathbf{n} \equiv w \quad (2.13)$$

Let us postulate that the water velocity tangential to the surface  $\Gamma$  is equal on both sides of  $\Gamma$ :

$$(\mathbf{v}_f - \mathbf{v}_1)_\parallel = (\mathbf{v}_2 - \mathbf{v}_1)_\parallel \equiv \mathbf{q} \quad (2.14)$$

Note that  $\mathbf{q}$  is a vector that is tangent to the membrane. It is easily checked that the boundary conditions (2.13) and (2.14) lead to conservation of fluid in the whole region  $\mathbb{U}$ .

Force balance across the interface  $\Gamma$  is given as follows.

$$(\mathcal{T}_f + \mathcal{S}_f)\mathbf{n} - (\mathcal{T}_1 + \mathcal{T}_2 + \mathcal{S}_g)\mathbf{n} + [p]\mathbf{n} = 0, \quad [p] = p|_{\Omega_t} - p|_{\mathcal{R}_t} \quad (2.15)$$

where  $\cdot|_{\Omega_t}$  and  $\cdot|_{\mathcal{R}_t}$  shall henceforth denote evaluation on the  $\Omega_t$  side and the  $\mathcal{R}_t$  side of  $\Gamma_t$  respectively. We also use the notation  $[\cdot] \equiv \cdot|_{\Omega_t} - \cdot|_{\mathcal{R}_t}$  to denote the jump in the enclosed quantity across  $\Gamma_t$ . In particular, we have:

$$((\mathcal{T}_f + \mathcal{S}_f)\mathbf{n} - (\mathcal{T}_1 + \mathcal{T}_2 + \mathcal{S}_g)\mathbf{n}) \cdot \mathbf{q} = 0 \quad (2.16)$$

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

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

$$\mathbf{v}_f = 0. \quad (2.17)$$

At this point, we have the boundary conditions (2.14), (2.13) and (2.15) on  $\Gamma$ , which together give us six boundary conditions. Mass balance and total force balance would provide the necessary number of boundary conditions if the interior of  $\Omega_t$  were composed of a one-phase medium. Here, the interior of  $\Omega_t$  is a two-phase gel. We thus require additional boundary conditions. This will be discussed in subsequent sections.

We conclude this Section by stating a result that will be useful later in discussing free energy dissipation.

LEMMA 2.1. *Suppose  $\phi_i, \mathbf{v}_i, \mathbf{v}_f$  are smooth functions that satisfy (2.1), (2.2), (2.4), (2.9), (2.10), (2.13), (2.14), (2.15), (2.17) and suppose  $p_\Delta, \mathbf{f}_i, \mathbf{f}_f$  satisfy (2.6) and (2.11). We have:*

$$\begin{aligned} 0 = & - \int_{\Omega_t} ((\nabla \mathbf{v}_1) : \mathcal{T}_1 + (\nabla \mathbf{v}_2) : \mathcal{T}_2) d\mathbf{x} - \int_{\Omega_f} (\nabla \mathbf{v}_f) : \mathcal{T}_f d\mathbf{x} \\ & + \int_{\Omega_t} ((-\phi_1 \nabla p_\Delta + \mathbf{f}_1 + \mathbf{g}_1) \cdot \mathbf{v}_1 + (\mathbf{f}_2 + \mathbf{g}_2) \cdot \mathbf{v}_2) d\mathbf{x} + \int_{\mathcal{R}_t} \mathbf{f}_f \cdot \mathbf{v}_f d\mathbf{x} \quad (2.18) \\ & - \int_{\Gamma} (((\mathcal{S}_g - \mathcal{S}_f) \mathbf{n}) \cdot \mathbf{v}_1 + w \Pi_\perp + \mathbf{q} \cdot \Pi_\parallel) dS, \end{aligned}$$

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

$$\Pi_\perp = (\mathbf{n} \cdot (\mathcal{T}_f \mathbf{n})) - \left( \mathbf{n} \cdot \left( \frac{\mathcal{T}_2}{\phi_2} \right) \mathbf{n} \right) + [p]. \quad (2.19)$$

*Proof.* Multiply (2.4) by  $\mathbf{v}_i$  and integrate over  $\Omega_t$ . Likewise, multiply (2.9) by  $\mathbf{v}_f$  and integrate over  $\mathcal{R}_t$ . Adding these expressions, we have

$$\begin{aligned} 0 = & \int_{\Omega_t} (\mathbf{v}_1 (\nabla \cdot \mathcal{T}_1) + \mathbf{v}_2 (\nabla \cdot \mathcal{T}_2)) d\mathbf{x} + \int_{\Omega_f} \mathbf{v}_f (\nabla \cdot \mathcal{T}_f) d\mathbf{x} \\ & + \int_{\Omega_t} ((-\phi_1 \nabla p_\Delta + \mathbf{f}_1 + \mathbf{g}_1) \cdot \mathbf{v}_1 + (\mathbf{f}_2 + \mathbf{g}_2) \cdot \mathbf{v}_2) d\mathbf{x} \\ & - \int_{\Omega_t} (\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) \cdot \nabla p d\mathbf{x} - \int_{\mathcal{R}_t} \mathbf{v}_f \cdot \nabla p d\mathbf{x} \quad (2.20) \\ = & - \int_{\Omega_t} ((\nabla \mathbf{v}_1) : \mathcal{T}_1 + (\nabla \mathbf{v}_2) : \mathcal{T}_2) d\mathbf{x} - \int_{\mathcal{R}_t} (\nabla \mathbf{v}_f) : \mathcal{T}_f d\mathbf{x} \\ & + \int_{\Omega_t} ((-\phi_1 \nabla p_\Delta + \mathbf{f}_1 + \mathbf{g}_1) \cdot \mathbf{v}_1 + (\mathbf{f}_2 + \mathbf{g}_2) \cdot \mathbf{v}_2) d\mathbf{x} \\ & + \int_{\Gamma_t} ((\mathcal{T}_1 \mathbf{n} - \phi_1 p \mathbf{n}) \cdot \mathbf{v}_1 + (\mathcal{T}_2 \mathbf{n} - \phi_2 p \mathbf{n}) \cdot \mathbf{v}_2 - (\mathcal{T}_f \mathbf{n} - p \mathbf{n}) \cdot \mathbf{v}_f) dS. \end{aligned}$$

where we used (2.3) and (2.10) in the second equality. Let us evaluate the last boundary integral. Using (2.13), (2.14) and (2.15), (2.16) we have:

$$\begin{aligned} & (\mathcal{T}_1 \mathbf{n} - \phi_1 p \mathbf{n}) \cdot \mathbf{v}_1 + (\mathcal{T}_2 \mathbf{n} - \phi_2 p \mathbf{n}) \cdot \mathbf{v}_2 - (\mathcal{T}_f \mathbf{n} - p \mathbf{n}) \cdot \mathbf{v}_f \\ = & ((\mathcal{T}_1 + \mathcal{T}_2) \mathbf{n} - \mathcal{T}_f \mathbf{n} - [p] \mathbf{n}) \cdot \mathbf{v}_1 \\ & + \left( \mathbf{n} \cdot \left( \frac{\mathcal{T}_2}{\phi_2} \right) \mathbf{n} - \mathbf{n} \cdot (\mathcal{T}_f \mathbf{n}) - [p] \right) w + (\mathcal{T}_2 \mathbf{n} - \mathcal{T}_f \mathbf{n}) \cdot \mathbf{q} \quad (2.21) \\ = & - ((\mathcal{S}_g - \mathcal{S}_f) \mathbf{n}) \cdot \mathbf{v}_1 + \left( \mathbf{n} \cdot \left( \frac{\mathcal{T}_2}{\phi_2} \right) \mathbf{n} - \mathbf{n} \cdot (\mathcal{T}_f \mathbf{n}) - [p] \right) w - (\mathcal{T}_1 \mathbf{n}) \cdot \mathbf{q}. \end{aligned}$$

This yields (2.18).  $\square$

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

$$\mathbf{x} = \varphi_t(\mathbf{X}). \quad (3.1)$$

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

$$\mathbf{v}_1(\varphi_t(\mathbf{X}), t) = \frac{\partial}{\partial t}(\varphi_t(\mathbf{X})). \quad (3.2)$$

We let  $F = \nabla_{\mathbf{X}}\varphi_t$  be the deformation gradient, where  $\nabla_{\mathbf{X}}$  denotes the gradient with respect to the reference coordinate. Define  $\mathcal{F} = F \circ \varphi_t^{-1}$  so that  $\mathcal{F}$  is the deformation gradient evaluated in  $\Omega_t$  rather than in  $\Omega$ . It is a direct consequence of (3.2) that  $F$  satisfies the following transport equation:

$$\frac{\partial F}{\partial t} \Big|_{\mathbf{X}=\varphi_t^{-1}(\mathbf{x})} = \frac{\partial \mathcal{F}}{\partial t} + (\mathbf{v}_1 \cdot \nabla)\mathcal{F} = (\nabla \mathbf{v}_1)\mathcal{F}. \quad (3.3)$$

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

$$(\phi_1 \circ \varphi_t)\det F = \phi_I \quad (3.4)$$

where  $\phi_I$  is a function defined on  $\Omega$  that takes values between 0 and 1. This should be clear from the meaning of the deformation gradient, but can also be checked directly using (3.3) and (2.2). The function  $\phi_I$  is the volume fraction of the polymer component in the reference configuration.

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

$$\begin{aligned} \mathcal{T}_1 &= \mathcal{T}_1^{\text{visc}} + \mathcal{T}_1^{\text{elas}}, \\ \mathcal{T}_1^{\text{visc}} &= \eta_1(\nabla \mathbf{v}_1 + (\nabla \mathbf{v}_1)^T), \quad \mathcal{T}_1^{\text{elas}} = \phi_1 \frac{\partial \mathcal{W}_{\text{elas}}(\mathcal{F})}{\partial \mathcal{F}} \mathcal{F}^T. \end{aligned} \quad (3.5)$$

The viscosity  $\eta_1 > 0$  may be a function of  $\phi_1$ , in which case we assume this function is smooth and bounded. The function  $\phi_1 \mathcal{W}_{\text{elas}}$  is the elastic energy per unit volume. An example form of  $\mathcal{W}_{\text{elas}}$  is given by [39]:

$$\mathcal{W}_{\text{elas}} = \mu_E \left( \frac{1}{2p} (\|F\|^{2p} - \|I\|^{2p}) + \frac{\|I\|^{2(p-1)}}{\beta} ((\det F)^{-\beta} - 1) \right), \quad p \geq 1, \quad (3.6)$$

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

The pressure difference  $p_\Delta$  is given as follows:

$$p_\Delta = \frac{d\mathcal{W}_{\text{FH}}}{d\phi_1}, \quad \mathcal{W}_{\text{FH}} = \frac{k_B T}{v_s} \left( \frac{v_s}{v_p} \phi_1 \ln \phi_1 + \phi_2 \ln \phi_2 + \chi \phi_1 \phi_2 \right). \quad (3.7)$$

The function  $\mathcal{W}_{\text{FH}}$  is the Flory-Huggins mixing energy where  $k_B T$  is the Boltzmann constant times absolute temperature,  $v_p$  and  $v_s$  are the volume occupied by a single molecule of polymer and solvent respectively and  $\chi$  is a parameter that describes the interaction energy between the polymer and solvent. Since  $v_s \ll v_p$  for a crosslinked polymer network, the first term in  $\mathcal{W}_{\text{FH}}$  is often taken to be 0. By substituting  $\phi_2 = 1 - \phi_1$  from (2.1), we may view  $\mathcal{W}_{\text{FH}}$  as a function only of  $\phi_1$ .

Given that  $\mathcal{W}_{\text{FH}}$  is a mixing energy, it does not “belong” to either the solvent or the polymer phase. This is reflected in the fact that the pressure difference  $p_\Delta$  is symmetric with respect to the role played by the polymer and solvent components in the following sense:

$$p_\Delta = p_1 - p_2 = \frac{d\mathcal{W}_{\text{FH}}}{d\phi_1} = -\frac{d\mathcal{W}_{\text{FH}}}{d\phi_2} = -(p_2 - p_1), \quad (3.8)$$

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

We let:

$$\mathbf{f}_1 = \mathbf{f}_2 = 0. \quad (3.9)$$

If we set

$$\mathcal{S}_g = \mathcal{S}_g^{\text{FH}} \equiv \left( \mathcal{W}_{\text{FH}}(\phi_1) - \phi_1 \frac{d}{d\phi_1} \mathcal{W}_{\text{FH}}(\phi_1) \right) I, \quad (3.10)$$

we find that (2.6) is satisfied.

We point out that there is some arbitrariness in what we call the pressure difference and what we call the stress. Indeed we may prescribe  $\mathcal{T}_1$  and  $p_\Delta$  as follows to obtain exactly the same equations as is obtained when using (3.5) and (3.7):

$$\mathcal{T}_1 = \mathcal{T}_1^{\text{visc}} + \mathcal{T}_1^{\text{elas}} + \mathcal{S}_g^{\text{FH}}, \quad p_\Delta = 0 \quad (3.11)$$

where  $I$  is the  $3 \times 3$  identity matrix. Though mathematically equivalent, we find (3.5) and (3.7) more physically appealing since the polymer and solvent phases are treated symmetrically as far as the Flory-Huggins energy is concerned.

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

$$\mathbf{g}_1 = \mathbf{g}_{\text{fric}} = -\kappa(\mathbf{v}_1 - \mathbf{v}_2), \quad \mathbf{g}_2 = -\mathbf{g}_{\text{fric}}. \quad (3.12)$$

Here,  $\kappa > 0$  is the friction coefficient and may depend on  $\phi_1$ . Note that (2.8) is satisfied, and we thus have local force balance.

We assume that the fluid is viscous:

$$\mathcal{T}_{2,f} = \eta_{2,f} (\nabla \mathbf{v}_{2,f} + (\nabla \mathbf{v}_{2,f})^T). \quad (3.13)$$

The viscosity  $\eta_f > 0$  is a constant and  $\eta_2 > 0$  may be a (smooth and bounded) function of  $\phi_2$  (or equivalently,  $\phi_1$ ). For the body force, in the fluid, we let:

$$\mathbf{f}_f = 0, \quad \mathcal{S}_f = 0. \quad (3.14)$$

Condition (2.11) is trivially satisfied with the above definitions of  $\mathbf{f}_f$  and  $\mathcal{S}_f$ .

We now turn to boundary conditions. As was mentioned in the previous section, (2.13), (2.14) and (2.15) provide only six boundary conditions. We need three boundary conditions for each of the components in contact with the interface  $\Gamma_t$ . We have

three components, the polymer and solvent components of the gel and the surrounding fluid. We thus need nine boundary conditions. We now specify the remaining three boundary conditions. They are:

$$\eta_{\perp} w = \Pi_{\perp}, \quad (3.15)$$

$$\eta_{\parallel} \mathbf{q} = \Pi_{\parallel} \equiv (\mathcal{T}_1 \mathbf{n})_{\parallel}, \quad (3.16)$$

where  $\Pi_{\perp}$  was defined in (2.19) and  $\eta_{\perp}$  and  $\eta_{\parallel}$  are positive constants. We point out that  $\Pi_{\perp}$  should be interpreted as the difference in fluid normal stresses across the gel-fluid interface. Equation (3.15) thus states that fluid flow across the gel-fluid interface is proportional to this normal fluid stress difference. If we set  $\eta_{\perp} = 0$ , there is no interfacial friction for water flow and the normal fluid stresses balance. If we set  $\eta_{\perp} \rightarrow \infty$ ,  $w = 0$  and the gel-fluid interface is impermeable to fluid flow. Condition (3.16) is a Navier-type slip boundary condition. If  $\eta_{\parallel} \rightarrow \infty$ , this amounts to taking  $\mathbf{q} = 0$ . This will give us a tangential no-slip boundary condition for the fluid.

The following result states that the total free energy, given as the sum of the polymer elastic energy  $E_{\text{elas}}$ , the Flory-Huggins mixing energy  $E_{\text{FH}}$ , decreases through viscous or frictional dissipation in the bulk ( $I_{\text{visc}}$ ) and on the interface ( $J_{\text{visc}}$ ).

**THEOREM 3.1.** *Let  $\phi_i, \mathbf{v}_i$ , and  $\mathbf{v}_f$ , be smooth functions that satisfy (2.1), (2.2), (2.4), (2.9), (2.10), (2.13), (2.14), (2.15), (2.17), (3.15), (3.16) where the stress tensors, pressure difference and body forces are given by (3.5), (3.13), (3.7), (3.9), (3.12) and (3.14). Then, we have free energy dissipation in the following sense:*

$$\begin{aligned} \frac{d}{dt} (E_{\text{elas}} + E_{\text{FH}}) &= -I_{\text{visc}} - J_{\text{visc}}, \\ E_{\text{elas}} &= \int_{\Omega_t} \phi_1 \mathcal{W}_{\text{elas}}(\mathcal{F}) d\mathbf{x}, \quad E_{\text{FH}} = \int_{\Omega_t} \mathcal{W}_{\text{FH}}(\phi_1) d\mathbf{x}, \\ I_{\text{visc}} &= \int_{\Omega_t} \left( \sum_{i=1}^2 2\eta_i \|\nabla_S \mathbf{v}_i\|^2 + \kappa |\mathbf{v}_1 - \mathbf{v}_2|^2 \right) d\mathbf{x} + \int_{\mathcal{R}_t} 2\eta_f \|\nabla_S \mathbf{v}_f\|^2 d\mathbf{x}, \\ J_{\text{visc}} &= \int_{\Gamma_t} \left( \eta_{\perp} w^2 + \eta_{\parallel} |\mathbf{q}|^2 \right) dS, \end{aligned} \quad (3.17)$$

where  $\nabla_S$  is the symmetric part of the corresponding velocity gradient and  $\|\cdot\|$  denotes the Frobenius norm of the  $3 \times 3$  matrix.

*Proof.* We can prove (3.17) by a direct application of Lemma 2.1. Substitute (3.5), (3.13), (3.7), (3.9), (3.12), (3.14), (3.15) and (3.16) into (2.18). We see that (3.17) is immediate if we can show the following two identities:

$$\frac{d}{dt} \int_{\Omega_t} \phi_1 \mathcal{W}_{\text{elas}}(\mathcal{F}) d\mathbf{x} = \int_{\Omega_t} (\nabla \mathbf{v}_1) : \mathcal{T}_1^{\text{elas}} d\mathbf{x}, \quad (3.18)$$

$$\begin{aligned} \frac{d}{dt} \int_{\Omega_t} \mathcal{W}_{\text{FH}}(\phi_1) d\mathbf{x} &= \int_{\Gamma_t} ((\mathcal{S}_g - \mathcal{S}_f) \mathbf{n}) \cdot \mathbf{v}_1 dS \\ &\quad - \int_{\Omega_t} ((-\phi_1 \nabla p_{\Delta} + \mathbf{f}_1) \cdot \mathbf{v}_1 + \mathbf{f}_2 \cdot \mathbf{v}_2) d\mathbf{x}. \end{aligned} \quad (3.19)$$



First consider (3.18):

$$\begin{aligned}
& \frac{d}{dt} \int_{\Omega_t} \phi_1 \mathcal{W}_{\text{elas}}(\mathcal{F}) d\mathbf{x} = \frac{d}{dt} \int_{\Omega} \phi_I \mathcal{W}_{\text{elas}}(F) d\mathbf{X} \\
& = \int_{\Omega} \phi_I \frac{\partial \mathcal{W}_{\text{elas}}(F)}{\partial F} : \frac{\partial F}{\partial t} d\mathbf{X} = \int_{\Omega_t} \phi_1 \frac{\partial \mathcal{W}_{\text{elas}}(\mathcal{F})}{\partial \mathcal{F}} : (\nabla \mathbf{v}_1 \mathcal{F}) d\mathbf{x} \quad (3.20) \\
& = \int_{\Omega_t} \left( \phi_1 \frac{\partial \mathcal{W}_{\text{elas}}(\mathcal{F})}{\partial \mathcal{F}} \mathcal{F}^T \right) : (\nabla \mathbf{v}_1) d\mathbf{x} = \int_{\Omega_t} (\nabla \mathbf{v}_1) : \mathcal{T}_1^{\text{elas}} d\mathbf{x},
\end{aligned}$$

where we used (3.4) in the first and third equalities and (3.3) in the third equality. Let us now evaluate the right hand side of (3.19):

$$\begin{aligned}
& \int_{\Gamma_t} (\mathcal{S}_g \mathbf{n}) \cdot \mathbf{v}_1 dS + \int_{\Omega_t} (\phi_1 \nabla p_{\Delta}) \cdot \mathbf{v}_1 d\mathbf{x} \\
& = \int_{\Gamma_t} \left( \mathcal{W}_{\text{FH}} - \phi_1 \frac{d\mathcal{W}_{\text{FH}}}{d\phi_1} \right) \mathbf{v}_1 \cdot \mathbf{n} dS + \int_{\Omega_t} \left( \phi_1 \mathbf{v}_1 \cdot \nabla \left( \frac{d\mathcal{W}_{\text{FH}}}{d\phi_1} \right) \right) d\mathbf{x} \quad (3.21) \\
& = \int_{\Gamma_t} (\mathcal{W}_{\text{FH}}) \mathbf{v}_1 \cdot \mathbf{n} dS + \int_{\Omega_t} \left( \frac{d\mathcal{W}_{\text{FH}}}{d\phi_1} \frac{\partial \phi_1}{\partial t} \right) d\mathbf{x} = \frac{d}{dt} \int_{\Omega_t} \mathcal{W}_{\text{FH}} d\mathbf{x},
\end{aligned}$$

where we integrated by parts and used (2.2) in the second equality.  $\square$

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

$$\mathcal{W}_{\text{ion}} = k_B T \sum_{k=1}^N c_k \ln c_k, \quad (4.1)$$

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

$$\mu_k = \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} + q z_k \psi = k_B T \ln c_k + q z_k \psi + k_B T. \quad (4.2)$$

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

$$\begin{aligned}
& \frac{\partial}{\partial t} (\phi_2 c_k) + \nabla \cdot (\mathbf{v}_2 \phi_2 c_k) = \nabla \cdot \left( \frac{D_k c_k}{k_B T} \nabla \mu_k \right) \\
& = \nabla \cdot \left( D_k \left( \nabla c_k + \frac{q z_k c_k}{k_B T} \nabla \psi \right) \right), \quad (4.3)
\end{aligned}$$

where  $D_k > 0, k = 1, \dots, N$  are the diffusion coefficients of the ions. The diffusion coefficients may be functions of  $\phi_2$ , in which case we suppose that they are smooth

bounded functions of  $\phi_2$ . Note that the choice (4.1) for  $\mathcal{W}_{\text{ion}}$  leads to linear diffusion. We point out here that our choice of the function  $\mathcal{W}_{\text{ion}}$  resulted in ionic diffusion being proportional to the gradient of  $c_k$ , not  $\phi_2 c_k$ . Recall that  $c_k$  is the concentration per unit solvent volume whereas  $\phi_2 c_k$  is concentration per unit volume. There are models in the literature in which ionic diffusion is proportional to the gradient of  $\phi_2 c_k$  instead of  $c_k$ . Our choice stems from the view that, since ions are dissolved in water (solvent), it can only diffuse within the water phase. We also point out that we do not include the effects of ion recombination, such as the protonation and de-protonation of charged polymeric side chains.

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

$$\frac{\partial c_k}{\partial t} + \nabla \cdot (\mathbf{v}_f c_k) = \nabla \cdot \left( \frac{D_k c_k}{k_B T} \nabla \mu_k \right). \quad (4.4)$$

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

$$-\nabla \cdot (\epsilon \nabla \psi) = \begin{cases} \phi_1 \rho_p + \sum_{k=1}^N q z_k \phi_2 c_k & \text{in } \Omega_t \\ \sum_{k=1}^N q z_k c_k & \text{in } \mathcal{R}_t \end{cases} \quad (4.5)$$

where  $\epsilon$  is the dielectric constant. The dielectric constant in the gel  $\Omega_t$  may well be different from that inside  $\mathcal{R}_t$ . We assume that  $\epsilon$  may be a (smooth and bounded) function of  $\phi_1$  in  $\Omega_t$  and remains constant in  $\mathcal{R}_t$ .

If we set the advective velocities to 0, equations (4.3), (4.4) and (4.5) are nothing other than the Poisson-Nernst-Planck system [41]. In many practical cases, the dielectric constant is “small” and it is an excellent approximation to let  $\epsilon \rightarrow 0$  in the above. We shall discuss this electroneutral limit in Section 5.

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

$$\begin{aligned} \mathbf{f}_1 &= \mathbf{f}_1^{\text{elec}} = -\rho_p \phi_1 \nabla \psi, \\ \mathbf{f}_2 &= \mathbf{f}_2^{\text{elec}} = - \left( \sum_{k=1}^N q z_k \phi_2 c_k \right) \nabla \psi, \\ \mathbf{f}_f &= \mathbf{f}_f^{\text{elec}} = - \left( \sum_{k=1}^N q z_k c_k \right) \nabla \psi. \end{aligned} \quad (4.6)$$

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

$$p_\Delta = p_\Delta^{\text{FH}} + p_\Delta^{\text{elec}}, \quad p_\Delta^{\text{FH}} = \frac{d\mathcal{W}_{\text{FH}}}{d\phi_1}, \quad p_\Delta^{\text{elec}} = -\frac{1}{2} \frac{d\epsilon}{d\phi_1} |\nabla \psi|^2. \quad (4.7)$$

The term  $p_\Delta^{\text{elec}}$  is known as the Helmholtz force [30]. We point out that the definition of  $p_\Delta^{\text{elec}}$  is symmetric with respect to  $\phi_1$  and  $\phi_2$ , as can be seen by an argument identical to (3.8).

Prescription (4.7) of  $p_\Delta$  assumes that  $p_\Delta$  can be separated into  $p_\Delta^{\text{FH}}$ , the mixing contribution, and  $p_\Delta^{\text{elec}}$ , the dielectric contribution. The interaction of ions and the charged polymeric side chains enters only through the electrostatic potential determined by the Poisson equation (4.5) (or the electroneutrality condition (5.15) if we

take the electroneutral limit, see Section 5). Our treatment does not take into account interactions between the solvent ions and the charged polymeric side chains beyond the above mean field effects, in line with classical mean field treatments of the statics of polyelectrolyte gels [38, 42]. Counterion condensation is such an effect, which may be significant especially at high ionic concentrations. Our use of  $\mathcal{W}_{\text{FH}}$  as the interaction energy between charged polymer and solvent is thus an approximation that may be valid only in relatively low ionic concentrations.

With the following definitions for  $\mathcal{S}_g$  and  $\mathcal{S}_f$ , conditions (2.11) and (2.6) are satisfied.

$$\begin{aligned}\mathcal{S}_g &= \mathcal{S}_g^{\text{FH}} + \mathcal{S}_g^{\text{elec}}, \quad \mathcal{S}_g^{\text{elec}} = \mathcal{S}_g^{\text{mw}} + \frac{1}{2}\phi_1 \frac{d\epsilon}{d\phi_1} |\nabla\psi|^2 I, \\ \mathcal{S}_f &= \mathcal{S}_f^{\text{elec}} = \mathcal{S}_f^{\text{mw}}, \quad \mathcal{S}_{g,f}^{\text{mw}} \equiv \epsilon \left( \nabla\psi \otimes \nabla\psi - \frac{1}{2} |\nabla\psi|^2 I \right)\end{aligned}\tag{4.8}$$

where  $\mathcal{S}_g^{\text{FH}}$  was given in (3.10). The tensor  $\mathcal{S}^{\text{mw}}$  is the standard Maxwell stress tensor in the absence of a magnetic field [30, 24]. Inside the gel there is an additional term to account for the non-uniformity of the dielectric constant. We prescribe  $\mathbf{g}_i$  as in (3.12). We also adopt the boundary conditions (3.15) and (3.16).

We must provide (4.3), (4.4) and (4.5) with boundary conditions. We require that the ionic concentrations  $c_k$  the flux across  $\Gamma_t$  be continuous:

$$\begin{aligned}[c_k] &= 0, \\ \left( (\mathbf{v}_f - \mathbf{v}_1)c_k - \frac{D_k c_k}{k_B T} \nabla\mu_k \right) \cdot \mathbf{n} \Big|_{\mathcal{R}_t} &= \left( (\mathbf{v}_2 - \mathbf{v}_1)\phi_2 c_k - \frac{D_k c_k}{k_B T} \nabla\mu_k \right) \cdot \mathbf{n} \Big|_{\Omega_t} \equiv j_k.\end{aligned}\tag{4.9}$$

We have named the concentration flux  $j_k$  for later convenience.

For the electrostatic potential  $\psi$ , we require:

$$[\psi] = [\epsilon \nabla\psi \cdot \mathbf{n}] = 0.\tag{4.11}$$

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

$$\left( \mathbf{v}_f c_k - \frac{D_k c_k}{k_B T} \nabla\mu_k \right) \cdot \mathbf{n} = 0,\tag{4.12}$$

$$\epsilon \nabla\psi \cdot \mathbf{n} = 0.\tag{4.13}$$

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

$$\int_{\mathcal{R}_t} \left( \sum_{k=1}^N q z_k c_k \right) d\mathbf{x} + \int_{\Omega_t} \left( \sum_{k=1}^N q z_k c_k + \rho_p \phi_1 \right) d\mathbf{x} = 0.\tag{4.14}$$

The electrostatic potential  $\psi$  is only determined up to an additive constant. Given that the amount of ions and the amount of polymer (integral of  $\phi_1$ ) are conserved, the above condition will be satisfied so long as it is satisfied at the initial time.

We now turn to linear momentum and free energy balance. We point out that a related energy identity for a different system was proved recently in [36].

THEOREM 4.1. Let  $\phi_i, \mathbf{v}_i$  and  $\mathbf{v}_f$  be smooth functions satisfying (2.1), (2.2), (2.4), (2.9), (2.10), (2.13), (2.14), (2.15), (2.17), (3.15), (3.16) and  $c_k$  and  $\psi$  are smooth functions satisfying (4.3), (4.4), (4.5), (4.10) and (4.11). Suppose the stress, pressure difference and the body forces are given by (3.5), (3.13), (4.7), (4.6) and (3.12). Then, we have the following free energy dissipation identity:

$$\begin{aligned} \frac{d}{dt}(E_{\text{elas}} + E_{\text{FH}} + E_{\text{ion}} + E_{\text{elec}}) &= -I_{\text{visc}} - I_{\text{diff}} - J_{\text{visc}}, \\ E_{\text{ion}} &= \int_{\Omega_t} \phi_2 \mathcal{W}_{\text{ion}} d\mathbf{x} + \int_{\mathcal{R}_t} \mathcal{W}_{\text{ion}} d\mathbf{x}, \quad E_{\text{elec}} = \int_{\mathbb{U}} \frac{1}{2} \epsilon |\nabla \psi|^2 d\mathbf{x}, \\ I_{\text{diff}} &= \int_{\mathbb{U}} \frac{D_k c_k}{k_B T} |\nabla \mu_k|^2 d\mathbf{x}, \end{aligned} \quad (4.15)$$

where  $E_{\text{elas}}, E_{\text{FH}}, I_{\text{visc}}$  and  $J_{\text{visc}}$  were defined in (3.17).

*Proof.* Substitute (3.5), (3.13)-(3.16) into (2.18), Using Lemma 2.1 and the results of Theorem 3.1, we have:

$$\begin{aligned} \frac{d}{dt}(E_{\text{elas}} + E_{\text{FH}}) &= -I_{\text{visc}} - J_{\text{visc}} + P_{\text{elec}}, \\ P_{\text{elec}} &= \int_{\Omega_t} (-\phi_1 \nabla p_{\Delta}^{\text{elec}} + \mathbf{f}_1^{\text{elec}}) \cdot \mathbf{v}_1 + \mathbf{f}_2^{\text{elec}} \cdot \mathbf{v}_2 d\mathbf{x} \\ &\quad + \int_{\mathcal{R}_t} \mathbf{f}_f^{\text{elec}} \cdot \mathbf{v}_f d\mathbf{x} - \int_{\Gamma_t} ((\mathcal{S}_g^{\text{elec}} - \mathcal{S}_f^{\text{elec}}) \mathbf{n}) \cdot \mathbf{v}_1 dS. \end{aligned} \quad (4.16)$$

Comparing this with (4.15), we must show that:

$$\frac{d}{dt}(E_{\text{ion}} + E_{\text{elec}}) = -I_{\text{diff}} - P_{\text{elec}}. \quad (4.17)$$

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

$$\begin{aligned} &\int_{\Omega_t} \rho_p \psi \left( \frac{\partial \phi_1}{\partial t} + \nabla \cdot (\phi_1 \mathbf{v}_1) \right) d\mathbf{x} \\ &= \frac{d}{dt} \int_{\Omega_t} \rho_p \phi_1 \psi d\mathbf{x} - \int_{\Omega_t} \rho_p \phi_1 \frac{\partial \psi}{\partial t} d\mathbf{x} + \int_{\Omega_t} \mathbf{f}_1^{\text{elec}} \cdot \mathbf{v}_1 d\mathbf{x} = 0, \end{aligned} \quad (4.18)$$

where we integrated by parts and used the fact that  $\rho_p$  is a constant. Note that we used (4.6) to rewrite the third integral in terms of  $\mathbf{f}_1^{\text{elec}}$ . Multiply (4.3) by  $\mu_k$  and integrate over  $\Omega_t$ . The left hand side gives:

$$\begin{aligned} &\int_{\Omega_t} \left( \sum_{k=1}^N \mu_k \left( \frac{\partial}{\partial t} (\phi_2 c_k) + \nabla \cdot (\mathbf{v}_2 \phi_2 c_k) \right) \right) d\mathbf{x} \\ &= \int_{\Omega_t} \left( \sum_{k=1}^N \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \left( \frac{\partial}{\partial t} (\phi_2 c_k) + \nabla \cdot (\mathbf{v}_2 \phi_2 c_k) \right) \right) d\mathbf{x} \\ &\quad + \int_{\Omega_t} \left( \sum_{k=1}^N q z_k \psi \left( \frac{\partial}{\partial t} (\phi_2 c_k) + \nabla \cdot (\mathbf{v}_2 \phi_2 c_k) \right) \right) d\mathbf{x} = S_1 + S_2. \end{aligned} \quad (4.19)$$

To simplify  $S_1$ , note that:

$$\begin{aligned} \sum_{k=1}^N \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \left( \frac{\partial}{\partial t} (\phi_2 c_k) + \nabla \cdot (\mathbf{v}_2 \phi_2 c_k) \right) &= \sum_{k=1}^N \phi_2 \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} \left( \frac{\partial c_k}{\partial t} + \mathbf{v}_2 \cdot \nabla c_k \right) \\ &= \phi_2 \left( \frac{\partial}{\partial t} \mathcal{W}_{\text{ion}} + \mathbf{v}_2 \cdot \nabla \mathcal{W}_{\text{ion}} \right) = \frac{\partial}{\partial t} (\phi_2 \mathcal{W}_{\text{ion}}) + \nabla \cdot (\mathbf{v}_2 \phi_2 \mathcal{W}_{\text{ion}}) \end{aligned} \quad (4.20)$$

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

$$\begin{aligned} S_1 &= \int_{\Omega_t} \frac{\partial}{\partial t} (\phi_2 \mathcal{W}_{\text{ion}}) + \nabla \cdot (\mathbf{v}_2 \phi_2 \mathcal{W}_{\text{ion}}) d\mathbf{x} \\ &= \frac{d}{dt} \int_{\Omega_t} \phi_2 \mathcal{W}_{\text{ion}} d\mathbf{x} + \int_{\Gamma_t} \phi_2 \mathcal{W}_{\text{ion}} (\mathbf{v}_2 - \mathbf{v}_1) \cdot \mathbf{n} dS. \end{aligned} \quad (4.21)$$

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

$$\begin{aligned} S_2 &= \frac{d}{dt} \int_{\Omega_t} \left( \psi \sum_{k=1}^N q z_k \phi_2 c_k \right) d\mathbf{x} - \int_{\Omega_t} \left( \frac{\partial \psi}{\partial t} \sum_{k=1}^N q z_k \phi_2 c_k \right) d\mathbf{x} \\ &\quad + \int_{\Omega_t} \mathbf{f}_2^{\text{elec}} \cdot \mathbf{v}_2 d\mathbf{x} + \int_{\Gamma_t} \left( \psi \sum_{k=1}^N q z_k c_k \phi_2 (\mathbf{v}_2 - \mathbf{v}_1) \cdot \mathbf{n} \right) d\mathbf{x}, \end{aligned} \quad (4.22)$$

where we used (4.6) to write the third integral in terms of  $\mathbf{f}_2^{\text{elec}}$ . If we multiply the right hand side of (4.3) by  $\mu_k$ , sum in  $k$  and integrate in  $\Omega_t$ , we have:

$$\begin{aligned} &\int_{\Omega_t} \left( \sum_{k=1}^N \mu_k \nabla \cdot \left( \frac{D_k c_k}{k_B T} \nabla \mu_k \right) \right) d\mathbf{x} \\ &= \int_{\Gamma_t} \left( \sum_{k=1}^N \mu_k \frac{D_k c_k}{k_B T} \nabla \mu_k \cdot \mathbf{n} \right) dS - \int_{\Omega_t} \left( \sum_{k=1}^N \frac{D_k c_k}{k_B T} |\nabla \mu_k|^2 \right) d\mathbf{x}. \end{aligned} \quad (4.23)$$

Collecting (4.18), (4.19), (4.21)-(4.23), we have:

$$\begin{aligned} &\frac{d}{dt} \int_{\Omega_t} \left( \phi_2 \mathcal{W}_{\text{ion}} + \psi \left( \phi_1 \rho_p + \sum_{k=1}^N q z_k \phi_2 c_k \right) \right) d\mathbf{x} \\ &- \int_{\Omega_t} \left( \frac{\partial \psi}{\partial t} \left( \phi_1 \rho_p + \sum_{k=1}^N q z_k \phi_2 c_k \right) \right) d\mathbf{x} \\ &= - \int_{\Gamma_t} \left( \sum_{k=1}^N j_k \mu_k - \left( \sum_{k=1}^N c_k \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} - \mathcal{W}_{\text{ion}} \right) w \right) dS \\ &- \int_{\Omega_t} \left( \sum_{k=1}^N \frac{D_k c_k}{k_B T} |\nabla \mu_k|^2 \right) d\mathbf{x} - \int_{\Omega_t} (\mathbf{f}_1^{\text{elec}} \cdot \mathbf{v}_1 + \mathbf{f}_2^{\text{elec}} \cdot \mathbf{v}_2) d\mathbf{x} \end{aligned} \quad (4.24)$$

where we used (2.13) and (4.10). Multiplying (4.4) by  $\mu_k$ , taking the sum in  $k$  and

integrating over  $\mathcal{R}_t$ , we obtain, similarly to (4.24):

$$\begin{aligned}
& \frac{d}{dt} \int_{\mathcal{R}_t} \left( \mathcal{W}_{\text{ion}} + \psi \sum_{k=1}^N q z_k c_k \right) d\mathbf{x} - \int_{\mathcal{R}_t} \left( \frac{\partial \psi}{\partial t} \sum_{k=1}^N q z_k c_k \right) d\mathbf{x} \\
&= \int_{\Gamma_t} \left( \sum_{k=1}^N j_k \mu_k - \left( \sum_{k=1}^N c_k \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} - \mathcal{W}_{\text{ion}} \right) w \right) dS \\
& - \int_{\mathcal{R}_t} \left( \sum_{k=1}^N \frac{D_k c_k}{k_B T} |\nabla \mu_k|^2 \right) d\mathbf{x} - \int_{\mathcal{R}_t} \mathbf{f}_f^{\text{elec}} \cdot \mathbf{v}_f d\mathbf{x}.
\end{aligned} \tag{4.25}$$

Adding (4.24) and (4.25) and using the fact that  $c_k$  and  $\psi$  are continuous across  $\Gamma_t$ , we have,:

$$\begin{aligned}
& \frac{d}{dt} E_{\text{ion}} - \frac{d}{dt} \int_{\mathbb{U}} \psi \nabla \cdot (\epsilon \nabla \psi) d\mathbf{x} + \int_{\mathbb{U}} \frac{\partial \psi}{\partial t} \nabla \cdot (\epsilon \nabla \psi) d\mathbf{x} \\
&= -I_{\text{diff}} - P_{\text{elec}} - \int_{\Omega_t} (\phi_1 \mathbf{v}_1) \cdot \nabla p_{\Delta}^{\text{elec}} d\mathbf{x} - \int_{\Gamma_t} ((\mathcal{S}_g^{\text{elec}} - \mathcal{S}_f^{\text{elec}}) \mathbf{n}) \cdot \mathbf{v}_1 dS.
\end{aligned} \tag{4.26}$$

Now consider the two integrals on the first line of (4.26):

$$-\frac{d}{dt} \int_{\mathbb{U}} \psi \nabla \cdot (\epsilon \nabla \psi) d\mathbf{x} = \frac{d}{dt} \int_{\mathbb{U}} \epsilon |\nabla \psi|^2 d\mathbf{x} + \frac{d}{dt} \int_{\Gamma_t} \left[ \psi \epsilon \frac{\partial \psi}{\partial \mathbf{n}} \right] dS = \frac{d}{dt} \int_{\mathbb{U}} \epsilon |\nabla \psi|^2 d\mathbf{x} \tag{4.27}$$

where we used the continuity of  $\psi$  and (4.11) in the second equality. Let us now turn to the second integral in the first line of (4.26)

$$\begin{aligned}
& \int_{\mathbb{U}} \frac{\partial \psi}{\partial t} \nabla \cdot (\epsilon \nabla \psi) d\mathbf{x} = - \int_{\mathbb{U}} \epsilon \nabla \psi \nabla \frac{\partial \psi}{\partial t} d\mathbf{x} + \int_{\Gamma_t} \left[ \epsilon \frac{\partial \psi}{\partial \mathbf{n}} \frac{\partial \psi}{\partial t} \right] dS \\
&= - \frac{d}{dt} \int_{\mathbb{U}} \frac{\epsilon}{2} |\nabla \psi|^2 d\mathbf{x} + \int_{\Omega_t} \frac{1}{2} \frac{\partial \epsilon}{\partial t} |\nabla \psi|^2 d\mathbf{x} + \int_{\Gamma_t} \left( \left[ \frac{\epsilon}{2} |\nabla \psi|^2 \right] \mathbf{v}_1 \cdot \mathbf{n} + \left[ \epsilon \frac{\partial \psi}{\partial \mathbf{n}} \frac{\partial \psi}{\partial t} \right] \right) dS \\
&= - \frac{d}{dt} \int_{\mathbb{U}} \frac{\epsilon}{2} |\nabla \psi|^2 d\mathbf{x} - \int_{\Omega_t} \frac{1}{2} \frac{d\epsilon}{d\phi_1} \nabla \cdot (\phi_1 \mathbf{v}_1) |\nabla \psi|^2 d\mathbf{x} \\
& + \int_{\Gamma_t} \left( \left[ \frac{\epsilon}{2} |\nabla \psi|^2 \right] \mathbf{v}_1 \cdot \mathbf{n} + \left[ \epsilon \frac{\partial \psi}{\partial \mathbf{n}} \frac{\partial \psi}{\partial t} \right] \right) dS \\
&= - \frac{d}{dt} \int_{\mathbb{U}} \frac{\epsilon}{2} |\nabla \psi|^2 d\mathbf{x} - \int_{\Omega_t} (\phi_1 \mathbf{v}_1) \cdot \nabla p_{\Delta}^{\text{elec}} d\mathbf{x} \\
& + \int_{\Gamma_t} \left( \left( \left[ \frac{\epsilon}{2} |\nabla \psi|^2 \right] - \frac{1}{2} \phi_1 \frac{d\epsilon}{d\phi_1} |\nabla \psi|^2 \right) \mathbf{v}_1 \cdot \mathbf{n} + \left[ \epsilon \frac{\partial \psi}{\partial \mathbf{n}} \frac{\partial \psi}{\partial t} \right] \right) dS
\end{aligned} \tag{4.28}$$

where we used (2.2) with  $i = 1$  in the first equality and used (4.7) in the third equality. Substituting (4.27) and (4.28) into (4.26), we have:

$$\begin{aligned}
& \frac{d}{dt} (E_{\text{ion}} + E_{\text{elec}}) + \int_{\Gamma_t} \left( \left( \left[ \frac{\epsilon}{2} |\nabla \psi|^2 \right] - \frac{1}{2} \phi_1 \frac{d\epsilon}{d\phi_1} |\nabla \psi|^2 \right) \mathbf{v}_1 \cdot \mathbf{n} + \left[ \epsilon \frac{\partial \psi}{\partial \mathbf{n}} \frac{\partial \psi}{\partial t} \right] \right) dS \\
&= -I_{\text{diff}} - P_{\text{elec}} - \int_{\Gamma_t} ((\mathcal{S}_g^{\text{elec}} - \mathcal{S}_f^{\text{elec}}) \mathbf{n}) \cdot \mathbf{v}_1 dS.
\end{aligned} \tag{4.29}$$

Using the definition of  $\mathcal{S}_{g,f}^{\text{elec}}$  in (4.8), the above reduces to:

$$\frac{d}{dt}(E_{\text{ion}} + E_{\text{elec}}) + \int_{\Gamma_t} \left[ \epsilon \frac{\partial \psi}{\partial \mathbf{n}} \frac{\partial \psi}{\partial t} + ((\epsilon \nabla \psi \otimes \nabla \psi) \mathbf{n}) \cdot \mathbf{v}_1 \right] dS = -I_{\text{diff}} - P_{\text{elec}}. \quad (4.30)$$

Let us examine the integrand in the above integral:

$$\left[ \epsilon \frac{\partial \psi}{\partial \mathbf{n}} \frac{\partial \psi}{\partial t} + ((\epsilon \nabla \psi \otimes \nabla \psi) \mathbf{n}) \cdot \mathbf{v}_1 \right] = \epsilon \frac{\partial \psi}{\partial \mathbf{n}} \left[ \frac{\partial \psi}{\partial t} + \mathbf{v}_1 \cdot \nabla \psi \right], \quad (4.31)$$

where we used (4.11). Note that the continuity of  $\psi$  across  $\Gamma_t$  (see (4.11)) implies that the jump on the right hand side must be 0 given that  $\mathbf{v}_1$  coincides with the velocity of  $\Gamma_t$ . We have thus shown (4.17) and this concludes the proof.  $\square$

## 5. Electroneutral Limit.

**5.1. Electroneutral Model and the Energy Identity.** To discuss the electroneutral limit, we first non-dimensionalize our system of equations. We first consider the scalar equations (2.2), (4.3)-(4.5). Introduce the primed dimensionless variables:

$$\begin{aligned} \mathbf{x} &= L\mathbf{x}', \quad \mathbf{v}_{1,2,f} = V_0 \mathbf{v}'_{1,2,f}, \quad t = \frac{L}{V_0} t', \quad D_k = D_0 D'_k, \\ c_k &= c_0 c'_k, \quad \psi = \frac{k_B T}{q} \psi', \quad \rho_p = q c_0 \rho'_p, \quad \epsilon = \epsilon_f \epsilon', \end{aligned} \quad (5.1)$$

where  $L$  is the characteristic length (the size of the gel) and  $c_0, V_0$  and  $D_0$  are the representative ionic concentration, velocity and diffusion coefficient respectively. We shall prescribe  $V_0$  in (5.9). The dielectric constant is scaled with respect to  $\epsilon_f$ , the dielectric constant of the fluid. The scalar equations (2.1), (2.2), (4.3)-(4.5), in dimensionless form, are as follows:

$$\phi_1 + \phi_2 = 1, \quad \frac{\partial \phi_i}{\partial t} + \nabla \cdot (\mathbf{v}_i \phi_i) = 0, \quad \text{in } \Omega_t, \quad (5.2)$$

$$\frac{\partial(\phi_2 c_k)}{\partial t} + \nabla \cdot (\phi_2 \mathbf{v}_2 c_k) = \text{Pe}^{-1} \nabla \cdot (D_k (\nabla c_k + c_k z_k \nabla \psi)) \quad \text{in } \Omega_t, \quad (5.3)$$

$$\frac{\partial c_k}{\partial t} + \nabla \cdot (\mathbf{v}_f c_k) = \text{Pe}^{-1} \nabla \cdot (D_k (\nabla c_k + c_k z_k \nabla \psi)) \quad \text{in } \mathcal{R}_t, \quad (5.4)$$

$$-\beta^2 \nabla \cdot (\epsilon \nabla \psi) = \begin{cases} \phi_1 \rho_p + \sum_{k=1}^N z_k \phi_2 c_k & \text{in } \Omega_t \\ \sum_{k=1}^N z_k c_k & \text{in } \mathcal{R}_t \end{cases}, \quad (5.5)$$

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

$$\text{Pe} = \frac{V_0}{D_0/L}, \quad \beta = \frac{r_d}{L}, \quad r_d = \sqrt{\frac{\epsilon k_B T/q}{q c_0}}. \quad (5.6)$$

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

The interface  $\Gamma_t$  moves according to (2.12), which can be made dimensionless by scaling  $v_\Gamma$  and  $\mathbf{v}_1$  with respect to  $V_0$ . The interface conditions to (5.3)-(5.5) at  $\Gamma_t$  are given by the following dimensionless forms of (4.9), (4.10) and (4.11):

$$[\psi] = [\epsilon \nabla \psi \cdot \mathbf{n}] = [c_k] = 0, \quad (5.7)$$

$$((\mathbf{v}_f - \mathbf{v}_1)c_k - D_k c_k \nabla \mu_k) \cdot \mathbf{n}|_{\mathcal{R}_t} = ((\mathbf{v}_2 - \mathbf{v}_1)\phi_2 c_k - D_k c_k \nabla \mu_k) \cdot \mathbf{n}|_{\Omega_t}, \quad (5.8)$$

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

We now make dimensionless the vector equations (2.4) and (2.9). Introduce the following primed dimensionless variables:

$$\begin{aligned} \kappa &= \kappa_0 \kappa', \quad \eta_{1,2} = \eta_f \eta'_{1,2}, \quad \eta_{\perp, \parallel} = \kappa_0 L \eta'_{\perp, \parallel}, \quad p = c_0 k_B T p', \\ p_\Delta^{\text{FH}} &= c_0 k_B T p_\Delta^{\text{FH}'}, \quad \mathcal{T}_1^{\text{elas}} = c_0 k_B T \mathcal{T}_1^{\text{elas}'}, \quad \mathcal{S}_g^{\text{FH}} = c_0 k_B T \mathcal{S}_g^{\text{FH}'}, \quad V_0 = \frac{c_0 k_B T}{\kappa_0 L}, \end{aligned} \quad (5.9)$$

where  $\kappa_0$  is the representative magnitude of the friction coefficient. We have used the characteristic pressure  $c_0 k_B T$  and  $\kappa_0$  to prescribe the characteristic velocity  $V_0$ . Equations (2.4) and (2.9) now take the following dimensionless form:

$$\begin{aligned} \nabla \cdot \mathcal{T}_1^{\text{elas}} + \zeta \nabla \cdot (\eta_1 (\nabla \mathbf{v}_1 + (\nabla \mathbf{v}_1)^T)) - \phi_1 \nabla (p + p_\Delta^{\text{FH}}) - \kappa (\mathbf{v}_1 - \mathbf{v}_2) \\ = \phi_1 \rho_p \nabla \psi - \beta^2 \phi_1 \nabla \left( \frac{1}{2} \frac{d\epsilon}{d\phi_1} |\nabla \psi|^2 \right) \text{ in } \Omega_t \end{aligned} \quad (5.10)$$

$$\zeta \nabla \cdot (\eta_2 (\nabla \mathbf{v}_2 + (\nabla \mathbf{v}_2)^T)) - \phi_2 \nabla p - \kappa (\mathbf{v}_2 - \mathbf{v}_1) = \sum_{k=1}^N z_k \phi_2 c_k \nabla \psi, \text{ in } \Omega_t, \quad (5.11)$$

$$\zeta \nabla \cdot (\nabla \mathbf{v}_f + (\nabla \mathbf{v}_f)^T) - \nabla p = \sum_{k=1}^N z_k c_k \nabla \psi, \text{ in } \mathcal{R}_t, \quad (5.12)$$

Expressions (3.12), (4.6) and (4.7) were used as expressions for  $\mathbf{f}_2$ ,  $\mathbf{g}_2$ ,  $\mathbf{f}_f$  and  $p_\Delta$ . The dimensionless variable  $\zeta = \eta_f / (\kappa_0 L^2)$  is the ratio between the characteristic viscous and frictional forces.

The interface conditions at  $\Gamma_t$  for (5.10)-(5.12) are given by (2.13), (2.14), (2.15), (3.15) and (3.16) in dimensionless form. Equations (2.13), (2.14) and (3.16) can be made dimensionless by rescaling the velocities  $w$  and  $\mathbf{q}$  (as well as  $\mathbf{v}_{1,2,f}$ ) are with respect to  $V_0$  so that  $w = V_0 w'$  and  $\mathbf{q} = V_0 \mathbf{q}'$ . Equations (2.15) and (3.15) take the following form:

$$\begin{aligned} & \left( \zeta (\nabla \mathbf{v}_f + (\nabla \mathbf{v}_f)^T) + \beta^2 \left( \nabla \psi \otimes \nabla \psi - \frac{1}{2} |\nabla \psi|^2 I \right) \right) \mathbf{n} - p|_{\mathcal{R}_t} \mathbf{n} \\ &= (\mathcal{T}_1^{\text{elas}} + \mathcal{S}_g^{\text{FH}} + \zeta \eta_1 (\nabla \mathbf{v}_1 + (\nabla \mathbf{v}_1)^T) + \zeta \eta_2 (\nabla \mathbf{v}_2 + (\nabla \mathbf{v}_2)^T)) \mathbf{n} - p|_{\Omega_t} \mathbf{n} \\ &+ \beta^2 \left( \epsilon \nabla \psi \otimes \nabla \psi - \frac{1}{2} \left( \epsilon - \phi_1 \frac{d\epsilon}{d\phi_1} \right) |\nabla \psi|^2 I \right) \mathbf{n}, \end{aligned} \quad (5.13)$$

$$\eta_\perp w = \Pi_\perp,$$

$$\Pi_\perp = [p] - \mathbf{n} \cdot \left( \zeta \frac{\eta_2}{\phi_2} (\nabla \mathbf{v}_2 + (\nabla \mathbf{v}_2)^T) \right) \mathbf{n} + \mathbf{n} \cdot \zeta (\nabla \mathbf{v}_f + (\nabla \mathbf{v}_f)^T) \mathbf{n}. \quad (5.14)$$

The boundary condition in the outer boundary of  $\mathbb{U}$  are given by (2.17), (4.12) and (4.13) in dimensionless form.



In many cases of practical interest, the Debye length  $r_d$  is small compared to the system size. We thus consider the limit  $\beta \rightarrow 0$ , while keeping the other dimensionless constants fixed. Let us consider the Poisson equation (5.5). Setting  $\beta = 0$ , we obtain the following electroneutrality condition:

$$\begin{aligned} \phi_1 \rho_p + \sum_{k=1}^N z_k \phi_2 c_k &= 0 \text{ in } \Omega_t, \\ \sum_{k=1}^N z_k c_k &= 0 \text{ in } \mathcal{R}_t. \end{aligned} \tag{5.15}$$

If we replace the Poisson equation by the above algebraic constraints, boundary conditions (4.11) (or the boundary conditions for  $\psi$  in (5.7)) or (4.13) can no longer be satisfied. This indicates that, as  $\beta \rightarrow 0$ , a boundary layer whose thickness is of order  $\beta$  (or  $r_d$  in dimensional terms) develops at the interface  $\Gamma_t$ , within which electroneutrality is violated. This is known as the Debye layer [40]. (A Debye layer does not develop at  $\partial\mathcal{U}$  given our choice of imposing no-flux boundary conditions for  $\psi$ .) Thus, in deriving the equations to be satisfied in the limit  $\beta \rightarrow 0$ , care must be taken to capture effects arising from the Debye layer. We refer to the resulting system as the *electroneutral model*. The system before taking this limit will be referred to as the *Poisson model*. In the rest of this Section, we state the equations and boundary conditions of electroneutral model, and establish the free energy identity satisfied by the model. In Section 5.2, we use matched asymptotic analysis at the Debye layer to derive the electroneutral model in the limit  $\beta \rightarrow 0$ .

Let us now describe the electroneutral model. As stated above, we replace (5.5) with the electroneutrality conditions (5.15). The electrostatic potential  $\psi$  evolves so that the electroneutrality constraint is satisfied everywhere at each time instant. Given the electroneutrality condition, the right hand side of (5.12), is now 0. All other bulk equations remain the same.

We turn to boundary conditions. We no longer have boundary conditions for  $\psi$  ((4.11) or (4.13)), as discussed above. Consider the boundary conditions for the ionic concentrations  $c_k$ . We continue to require the flux conditions (5.8) at  $\Gamma_t$  and (4.12) at  $\partial\mathcal{U}$ . We must, however, abandon condition (5.7), that  $c_k$  be continuous across  $\Gamma_t$ . If all the  $c_k$  were continuous across  $\Gamma_t$ , the electroneutrality condition (5.15) would imply that  $\phi_2 \rho_p$  must be 0. This cannot hold in general. Instead of continuity of  $c_k$ , we require continuity of the chemical potential  $\mu_k$  across  $\Gamma_t$ :

$$[\mu_k] = 0, \quad k = 1, \dots, N. \tag{5.16}$$

This is a standard condition imposed when the electroneutral approximation is used [41]. We shall discuss this condition in Section 5.2.

Let us turn to the boundary conditions for the vector equations. Boundary conditions (2.13), (2.14) and (3.16) at  $\Gamma_t$  remain the same, and we continue to require (2.17) at  $\partial\mathcal{U}$ . For boundary condition (5.13), we simply set  $\beta = 0$ , thereby eliminating stresses of electrostatic origin. The non-trivial modification concerns the boundary condition (5.14). We let:

$$\begin{aligned} \eta_\perp w &= \widehat{\Pi}_\perp, \quad \widehat{\Pi}_\perp = \Pi_\perp - \pi_{\text{osm}}, \\ \pi_{\text{osm}} &= \left[ \sum_{k=1}^N c_k \frac{\partial \mathcal{W}_{\text{ion}}}{\partial c_k} - \mathcal{W}_{\text{ion}} \right] = \sum_{k=1}^N [c_k]. \end{aligned} \tag{5.17}$$

where  $\mathcal{W}_{\text{ion}}$  defined in (4.1) has been made dimensionless by scaling with respect to  $k_B T$ . In physical dimensions,  $\pi_{\text{osm}}$  takes the form:

$$\pi_{\text{osm}} = k_B T \sum_{k=1}^N [c_k]. \quad (5.18)$$

This is nothing other than the familiar van't Hoff expression for osmotic pressure. Equation (5.17) thus states that water flow across the interface  $\Gamma_t$  is driven by the mechanical force difference as well as the osmotic pressure difference across  $\Gamma_t$ . We shall derive this condition using matched asymptotics in Section 5.2.

The electroneutral model described above satisfies the following energy identity.

**THEOREM 5.1.** *Let  $\phi_i, c_k$  and  $\psi$  be smooth functions satisfying (5.2)-(5.4), (5.15), with boundary conditions (5.16), (5.8), and (4.12) (in dimensionless form). Let  $\mathbf{v}_i$  and  $\mathbf{v}_f$  be smooth functions satisfying (5.10) with  $\beta = 0$ , (5.11) and (5.12). For boundary conditions, we require (5.13) with  $\beta = 0$  and (5.17) as well as (2.13), (2.14), (3.16) and (2.17) (in dimensionless form). Then, the following identity holds:*

$$\frac{d}{dt}(E_{\text{elas}} + E_{\text{FH}} + E_{\text{ion}}) = -I_{\text{visc}} - I_{\text{diff}} - J_{\text{visc}}, \quad (5.19)$$

where  $E_{\text{elas}}, E_{\text{FH}}, I_{\text{visc}}, J_{\text{visc}}, E_{\text{ion}}$  and  $I_{\text{diff}}$  are the suitably non-dimensionalized versions of the quantities defined in (3.17) and (4.15).

*Proof.* The proof is completely analogous to Theorem 4.1. Expressions (4.24) and (4.25) also hold in the electroneutral case. Let us now add (4.24) and (4.25). We find:

$$\frac{d}{dt}E_{\text{ion}} = \int_{\Gamma_t} \pi_{\text{osm}} w dS - I_{\text{diff}} - P_{\text{elec}} \quad (5.20)$$

where we used (5.15), (5.16), and the definition of  $\pi_{\text{osm}}$  in (5.17). Now, Theorem 3.1 yields:

$$\frac{d}{dt}(E_{\text{elas}} + E_{\text{FH}}) = - \int_{\Gamma_t} \left( \Pi_{\perp} w + \eta_{\parallel} |\mathbf{q}|^2 \right) dS - I_{\text{visc}} + P_{\text{elec}}. \quad (5.21)$$

The integral on the right hand side of the above is *not* equal to  $J_{\text{visc}}$  as defined in (3.17) since we have now adopted (5.17) instead of (3.15) as our boundary condition for  $w$ . Now, adding (5.20) and (5.21) and using (5.17), we obtain (5.19).  $\square$

The reader of the above proof will realize that (5.16) and (5.17) are the only conditions that will allow an energy dissipation relation of the type (5.19) to hold. It may be said that, in the limit as  $\beta \rightarrow 0$ , boundary conditions (5.16) and (5.17) are forced upon us by the requirement that the limiting system satisfy a free energy identity. It is interesting that we do indeed recover the classical van't Hoff expression for osmotic pressure if we adopt (4.1) as our expression for  $\mathcal{W}_{\text{ion}}$ . We also point out that the conditions for stationary state for the above equations reduce to the Donnan conditions first proposed in [38]. In this sense, our electroneutral model is a dynamic extension of the static calculations in [38].

**5.2. Matched Asymptotic Analysis.** We have seen above that boundary conditions (5.16) and (5.17) arise naturally from the requirement of free energy dissipation. The goal of this Section is to derive the limiting boundary conditions (5.16) and (5.17) by way of matched asymptotic analysis.

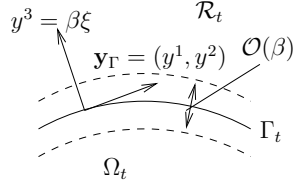


FIG. 5.1. *The Debye layer and the advected coordinate system. A boundary (or Debye) layer whose dimensionless thickness is on the order of  $\mathcal{O}(\beta)$ ,  $\beta = r_d/L$  forms near the gel-fluid interface  $\Gamma_t$ . The curvilinear coordinate system  $\mathbf{y} = (\mathbf{y}_\Gamma, y^3) = (y^1, y^2, y^3)$  advects with the surface  $\Gamma_t$ . The  $y^3$  direction is normal to  $\Gamma_t$ . A rescaled coordinate  $\xi = y^3/\beta$  is introduced to perform a matched asymptotic calculation.*

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

Given the presence of the boundary layer at  $\Gamma_t$ , we introduce a curvilinear coordinate system that conforms to and advects with  $\Gamma_t$  (Figure 5.1). Our first step is to rewrite the dimensionless Poisson model in this coordinate system using tensor calculus (see, for example, [3] or [2] for a treatment of tensor calculus in the context of continuum mechanics).

Introduce a local coordinate system  $\mathbf{y}_\Gamma = (y^1, y^2)$  on the initial surface  $\Gamma_0$  so that  $\mathbf{x}_\Gamma(\mathbf{y}_\Gamma, 0)$  gives the  $\mathbf{x}$ -coordinates of the surface  $\Gamma_0$ . Advect this coordinate system with the polymer velocity  $\mathbf{v}_1$ :

$$\frac{\partial \mathbf{x}_\Gamma}{\partial t} = \mathbf{v}_1. \quad (5.22)$$

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

Define the signed distance function:

$$y^3(\mathbf{x}, t) = \begin{cases} -\text{dist}(\mathbf{x}, \Gamma_t) & \text{if } \mathbf{x} \in \Omega_t, \\ \text{dist}(\mathbf{x}, \Gamma_t) & \text{if } \mathbf{x} \in \mathcal{R}_t. \end{cases} \quad (5.23)$$

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

$$\mathbf{x} = \mathcal{C}_t(\mathbf{y}), \text{ for } \mathbf{y} \in \mathcal{N} \subset \mathbb{R}^3 \quad (5.24)$$

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

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

$$g_{\sigma\tau} = \frac{\partial \mathcal{C}_t}{\partial y^\sigma} \cdot \frac{\partial \mathcal{C}_t}{\partial y^\tau}, \quad \sigma, \tau = 1, 2, 3. \quad (5.25)$$

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

$$g^{\sigma\alpha} g_{\alpha\tau} = \delta_\tau^\sigma \quad (5.26)$$

where  $\delta_\tau^\sigma$  is the Kronecker delta. In the above and henceforth, the summation convention is in effect for repeated Greek indices. Given (5.23), we have:

$$g_{33} = g^{33} = 1, \quad g_{\sigma 3} = g_{3\sigma} = g^{\sigma 3} = g^{\sigma 3} = 0 \text{ for } \sigma = 1, 2. \quad (5.27)$$

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

$$\Gamma_{\sigma\tau}^\alpha = \frac{1}{2} g^{\alpha\gamma} \left( \frac{\partial g_{\sigma\gamma}}{\partial y^\tau} + \frac{\partial g_{\tau\gamma}}{\partial y^\sigma} - \frac{\partial g_{\sigma\tau}}{\partial y^\gamma} \right). \quad (5.28)$$

From (5.27), it can be seen after some calculation that:

$$\Gamma_{3\sigma}^3 = 0 \text{ for } \sigma = 1, 2, 3. \quad (5.29)$$

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

$$\hat{\mathbf{v}} = \frac{\partial \mathcal{C}_t}{\partial t}. \quad (5.30)$$

We shall use the fact that:

$$\hat{\mathbf{v}}(\mathbf{y}_\Gamma, y_3 = 0) = \mathbf{v}_1, \quad (5.31)$$

which is just a restatement of (5.22). Finally, we assume the following condition on  $g_{\sigma\tau}$ :

$$g_{\sigma\tau}, g^{\sigma\tau}, \frac{\partial}{\partial y^\alpha} g_{\sigma\tau} \text{ remain bounded as } \beta \rightarrow 0. \quad (5.32)$$

This condition ensures that the surface  $\Gamma_t$  does not become increasingly ill-behaved as  $\beta \rightarrow 0$ , and ensures the presence of a boundary layer as  $\beta \rightarrow 0$ . In particular, this condition allows one to choose  $\mathcal{N}$  in (5.24) independent of  $\beta$ .

We rewrite equations (5.2)-(5.12) in the coordinate system  $(\mathbf{y}, t)$  instead of  $(\mathbf{x}, t)$ . Note that expressions involving the vector variables  $\mathbf{v} = \mathbf{v}_{1,2,f}$  or  $\hat{\mathbf{v}}$  must be rewritten in terms of  $(v^1, v^2, v^3)$ , the  $\mathbf{y}$ -components of the vector field, defined as follows:

$$\mathbf{v} = v^1 \frac{\partial \mathcal{C}_t}{\partial y^1} + v^2 \frac{\partial \mathcal{C}_t}{\partial y^2} + v^3 \frac{\partial \mathcal{C}_t}{\partial y^3}. \quad (5.33)$$

Let us first rewrite the scalar equations (5.2)-(5.5).

$$\phi_1 + \phi_2 = 1, \quad \frac{\partial \phi_i}{\partial t} - \hat{v}^\sigma \mathcal{D}_\sigma \phi_i + \mathcal{D}_\sigma(\phi_i v_i^\sigma) = 0, \text{ for } y^3 < 0 \quad (5.34)$$

$$\begin{aligned} \frac{\partial(\phi_2 c_k)}{\partial t} - \hat{v}^\sigma \mathcal{D}_\sigma(\phi_2 c_k) + \mathcal{D}_\sigma(\phi_2 c_k v_2^\sigma) \\ = \text{Pe}^{-1} g^{\sigma\tau} \mathcal{D}_\sigma(D_k(\mathcal{D}_\tau c_k + c_k z_k \mathcal{D}_\tau \psi)) \text{ for } y^3 < 0 \end{aligned} \quad (5.35)$$

$$\frac{\partial c_k}{\partial t} - \hat{v}^\sigma \mathcal{D}_\sigma c_k + \mathcal{D}_\sigma(c_k v_f^\sigma) = \text{Pe}^{-1} g^{\sigma\tau} \mathcal{D}_\sigma(D_k(\mathcal{D}_\tau c_k + c_k z_k \mathcal{D}_\tau \psi)) \text{ for } y^3 > 0 \quad (5.36)$$

$$-\beta^2 g^{\sigma\tau} \mathcal{D}_\sigma(\epsilon \mathcal{D}_\tau \psi) = \begin{cases} \phi_1 \rho_p + \sum_{k=1}^N z_k \phi_2 c_k & \text{for } y^3 < 0 \\ \sum_{k=1}^N z_k c_k & \text{for } y^3 > 0 \end{cases} \quad (5.37)$$

In the above,  $\mathcal{D}_\sigma$  is the covariant derivative with respect to  $y^\sigma$ . The function  $v_\Gamma$  is the magnitude of  $\mathbf{v}_\Gamma$  defined in (5.30). We need the boundary conditions (5.7):

$$\psi|_{y^3=0+} = \psi|_{y^3=0-}, \quad c_k|_{y^3=0+} = c_k|_{y^3=0-}, \quad \epsilon \frac{\partial \psi}{\partial y^3} \Big|_{y^3=0+} = \epsilon \frac{\partial \psi}{\partial y^3} \Big|_{y^3=0-} \quad (5.38)$$

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

We only need the vector equations for  $\mathbf{v}_2$  and  $\mathbf{v}_f$ . Equations (5.11) and (5.12) are rewritten as follows:

$$\begin{aligned} & \zeta(g^{\sigma\tau}\mathcal{D}_\sigma(\eta_2(\mathcal{D}_\tau v_2^\alpha)) + g^{\alpha\tau}\mathcal{D}_\sigma(\eta_2(\mathcal{D}_\tau v_2^\sigma))) - \phi_2 g^{\alpha\sigma}\mathcal{D}_\sigma p \\ &= \kappa(v_2^\alpha - v_1^\alpha) + \sum_{k=1}^N z_k \phi_2 c_k g^{\alpha\sigma}\mathcal{D}_\sigma \psi, \text{ for } y^3 < 0, \end{aligned} \quad (5.39)$$

$$\begin{aligned} & \zeta(g^{\sigma\tau}\mathcal{D}_\sigma(\mathcal{D}_\tau v_f^\alpha) + g^{\alpha\tau}\mathcal{D}_\sigma(\mathcal{D}_\tau v_f^\sigma)) - \phi_2 g^{\alpha\sigma}\mathcal{D}_\sigma p \\ &= \sum_{k=1}^N z_k c_k g^{\alpha\sigma}\mathcal{D}_\sigma \psi, \text{ for } y^3 > 0. \end{aligned} \quad (5.40)$$

We need boundary condition (5.14):

$$\eta_\perp w = p|_{y^3=0-} - p|_{y^3=0+} - 2\zeta \frac{\eta_2}{\phi_2} \frac{\partial v_2^3}{\partial y^3} + 2\zeta \frac{\partial v_f^3}{\partial y^3}. \quad (5.41)$$

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

$$c_k = c_k^0 + \beta c_k^1 + \dots, \quad v_1^\alpha = v_1^{\alpha,0} + \beta v_1^{\alpha,1} + \dots, \quad (5.42)$$

and likewise for other physical variables.

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

At the stationary state, all time derivatives are 0 and thus, the right hand side of the energy identity in (4.15) must be 0. From the condition that  $I_{\text{diff}} = 0$ , we see that  $\nabla \mu_k = 0$ . Given the continuity of  $c_k$  and  $\psi$  across  $\Gamma_t$ , we have:

$$\mu_k \text{ is constant throughout } \mathbb{U}. \quad (5.43)$$

This condition should persist in the limit  $\beta \rightarrow 0$ , and we have thus derived (5.16).

To derive (5.17), we first show that all velocities are identically equal to 0. Given  $I_{\text{visc}} = J_{\text{visc}} = 0$  and using the definitions of  $w$  and  $\mathbf{q}$  in  $J_{\text{visc}}$ , we have (see (3.17),(2.13) and (2.14)):

$$\nabla_S \mathbf{v}_f = 0 \text{ in } \mathcal{R}_t, \quad \nabla_S \mathbf{v}_2 = 0, \quad \mathbf{v}_1 = \mathbf{v}_2 \text{ in } \Omega_t, \quad (5.44)$$

$$\mathbf{v}_2 = \mathbf{v}_f \text{ on } \Gamma_t. \quad (5.45)$$

The vanishing of the symmetric gradient implies that  $\mathbf{v}_f$  and  $\mathbf{v}_2$  are velocity fields representing rigid rotation and translation. Given that  $\mathbf{v}_f = 0$  on  $\partial\mathbb{U}$ , we have  $\mathbf{v}_f = 0$  throughout  $\mathcal{R}_t$ . From (5.45), we see that  $\mathbf{v}_2 = 0$  on  $\Gamma_t = \partial\Omega_t$ , and we thus have  $\mathbf{v}_2 = 0$  throughout  $\Omega_t$ . From (5.44), we see that  $\mathbf{v}_1 = \mathbf{v}_2 = 0$  in  $\Omega_t$ .

We now examine equations (5.39) and (5.40). Given that all velocities are equal to 0, the leading order equations are:

$$-\frac{\partial p^0}{\partial \xi} = \sum_{k=1}^N z_k c_k^0 \frac{\partial \psi^0}{\partial \xi}, \text{ for } \xi < 0 \text{ and } \xi > 0. \quad (5.46)$$

The boundary conditions that we need at  $\xi = 0$  to leading order are (see (5.38) and (5.41)):

$$\lim_{\xi \rightarrow 0^-} c_k^0 = \lim_{\xi \rightarrow 0^+} c_k^0, \quad \lim_{\xi \rightarrow 0^-} \psi^0 = \lim_{\xi \rightarrow 0^+} \psi^0, \quad \lim_{\xi \rightarrow 0^-} p^0 = \lim_{\xi \rightarrow 0^+} p^0. \quad (5.47)$$

The matching conditions for the leading order terms are:

$$\begin{aligned} \lim_{\xi \rightarrow \pm\infty} c_k^0(\mathbf{y}_\Gamma, \xi) &= \lim_{y^3 \rightarrow 0^\pm} c_k^0(\mathbf{y}_\Gamma, y^3) \equiv c_{k,\pm}^0, \\ \lim_{\xi \rightarrow \pm\infty} \psi^0(\mathbf{y}_\Gamma, \xi) &= \lim_{y^3 \rightarrow 0^\pm} \psi^0(\mathbf{y}_\Gamma, y^3) \equiv \psi_\pm^0, \\ \lim_{\xi \rightarrow \pm\infty} p^0(\mathbf{y}_\Gamma, \xi) &= \lim_{y^3 \rightarrow 0^\pm} p^0(\mathbf{y}_\Gamma, y^3) \equiv p_\pm^0 \end{aligned} \quad (5.48)$$

Note that, given (5.43), we have:

$$\frac{\partial c_k^0}{\partial \xi} + z_k c_k^0 \frac{\partial \psi^0}{\partial \xi} = 0 \text{ for } \xi < 0 \text{ and } \xi > 0. \quad (5.49)$$

Integrating (5.46) from  $\xi = -\infty$  to  $\infty$ , we have:

$$\begin{aligned} p_+^0 - p_-^0 &= \int_{-\infty}^{\infty} \frac{\partial p^0}{\partial \xi} d\xi = - \sum_{k=1}^N \int_{-\infty}^{\infty} z_k c_k^0 \frac{\partial \psi^0}{\partial \xi} d\xi \\ &= \sum_{k=1}^N \int_{-\infty}^{\infty} \frac{\partial c_k^0}{\partial \xi} d\xi = \sum_{k=1}^N (c_{k,-}^0 - c_{k,+}^0). \end{aligned} \quad (5.50)$$

where we have used (5.47) and (5.48) in the first equality, (5.46) in the second equality, (5.49) in the third equality and (5.55) and (5.48) in the last equality. The above expression is nothing other than (5.17) where the velocities are taken to be 0.

**5.2.2. The Dynamic Case.** The dynamic case is somewhat more involved, but the essence of the derivation remains the same as in the equilibrium case. We derive (5.16) and (5.17) at points on  $\Gamma_t$  such that the water flow  $w$  does not vanish to leading order. This condition can equivalently be written as:

$$v_1^{3,0} \neq v_2^{3,0}. \quad (5.51)$$

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

We first derive (5.16). Explicitly write out the covariant derivatives in (5.36):

$$\begin{aligned} &\frac{\partial c_k}{\partial t} - \hat{v}^\sigma \frac{\partial c_k}{\partial y^\sigma} + \frac{\partial(c_k v_f^\sigma)}{\partial y^\sigma} + \Gamma_{\sigma\tau}^\sigma c_k v_f^\tau \\ &= \text{Pe}^{-1} g^{\sigma\tau} \left( \frac{\partial}{\partial y^\sigma} \left( D_k \frac{\partial c_k}{\partial y^\tau} + c_k z_k \frac{\partial \psi}{\partial y^\tau} \right) - \Gamma_{\sigma\tau}^\alpha \left( D_k \frac{\partial c_k}{\partial y^\alpha} + c_k z_k \frac{\partial \psi}{\partial y^\alpha} \right) \right). \end{aligned} \quad (5.52)$$

We now rescale  $y^3$  to  $\beta\xi$  to obtain the leading order equation in the inner layer. Given our assumption (5.32), the terms involving the Christoffel symbols  $\Gamma_{\sigma\tau}^\alpha$  do not make contributions to leading order. Using (5.27), we have, to leading order:

$$0 = \frac{\partial}{\partial \xi} \left( D_k \left( \frac{\partial c_k^0}{\partial \xi} + z_k c_k^0 \frac{\partial \psi^0}{\partial \xi} \right) \right) \text{ for } \xi > 0. \quad (5.53)$$

We may perform a similar calculation for (5.35) to obtain:

$$0 = \frac{\partial}{\partial \xi} \left( D_k \left( \frac{\partial c_k^0}{\partial \xi} + z_k c_k^0 \frac{\partial \psi^0}{\partial \xi} \right) \right) \text{ for } \xi < 0. \quad (5.54)$$

Note that the diffusion coefficient may be spatially non-constant for  $\xi < 0$  since  $D_k$  is in general a function of  $\phi_2$ . The boundary conditions that we need at  $\xi = 0$  to leading order are (see (5.38)):

$$\lim_{\xi \rightarrow 0^-} c_k^0 = \lim_{\xi \rightarrow 0^+} c_k^0, \quad \lim_{\xi \rightarrow 0^-} \psi^0 = \lim_{\xi \rightarrow 0^+} \psi^0. \quad (5.55)$$

The matching conditions for the leading order terms are:

$$\begin{aligned} \lim_{\xi \rightarrow \pm\infty} c_k^0(\mathbf{y}_\Gamma, \xi, t) &= \lim_{y^3 \rightarrow 0^\pm} c_k^0(\mathbf{y}_\Gamma, y^3, t) \equiv c_{k,\pm}^0, \\ \lim_{\xi \rightarrow \pm\infty} \psi^0(\mathbf{y}_\Gamma, \xi, t) &= \lim_{y^3 \rightarrow 0^\pm} \psi^0(\mathbf{y}_\Gamma, y^3, t) \equiv \psi_\pm^0, \end{aligned} \quad (5.56)$$

This suggests that the  $\xi$  derivatives of  $c_k^0$  and  $\psi^0$  should tend to 0 as  $\xi \rightarrow \pm\infty$ . Therefore, from (5.53) and (5.54) we have:

$$\frac{\partial c_k^0}{\partial \xi} + z_k c_k^0 \frac{\partial \psi^0}{\partial \xi} = 0, \quad (5.57)$$

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

$$\begin{aligned} & \lim_{y^3 \rightarrow 0^-} \mu_k^0(\mathbf{y}_\Gamma, y^3, t) - \lim_{y^3 \rightarrow 0^+} \mu_k^0(\mathbf{y}_\Gamma, y^3, t) \\ &= \lim_{\xi \rightarrow -\infty} \mu_k^0(\mathbf{y}_\Gamma, \xi, t) - \lim_{\xi \rightarrow \infty} \mu_k^0(\mathbf{y}_\Gamma, \xi, t) \\ &= - \int_{-\infty}^{\infty} \left( \frac{1}{c_k^0} \frac{\partial c_k^0}{\partial \xi} + z_k \frac{\partial \psi^0}{\partial \xi} \right) d\xi = 0. \end{aligned} \quad (5.58)$$

where we used the matching conditions (5.56) in the first equality and (5.55) in the second equality, and (5.57) in the last equality. We have thus derived (5.16).

We now turn to the derivation of (5.17). We first show that  $v_1^{3,0}, v_2^{3,0}, v_f^{3,0}, \phi_i^0$  are all independent of  $\xi$  in the inner layer. Equation (5.40) may be written explicitly as:

$$\begin{aligned} & \zeta g^{\sigma\tau} \left( \frac{\partial}{\partial y^\sigma} \left( \frac{\partial v_f^\alpha}{\partial y^\tau} + \Gamma_{\tau\gamma}^\alpha v^\gamma \right) + \Gamma_{\sigma\delta}^\alpha \left( \frac{\partial v_f^\delta}{\partial y^\tau} + \Gamma_{\tau\gamma}^\delta v^\gamma \right) - \Gamma_{\sigma\tau}^\delta \left( \frac{\partial v_f^\alpha}{\partial y^\delta} + \Gamma_{\delta\gamma}^\alpha v^\gamma \right) \right) \\ & + \zeta g^{\alpha\tau} \left( \frac{\partial}{\partial y^\sigma} \left( \frac{\partial v_f^\sigma}{\partial y^\tau} + \Gamma_{\tau\gamma}^\sigma v^\gamma \right) + \Gamma_{\sigma\delta}^\sigma \left( \frac{\partial v_f^\delta}{\partial y^\tau} + \Gamma_{\tau\gamma}^\delta v^\gamma \right) - \Gamma_{\sigma\tau}^\delta \left( \frac{\partial v_f^\sigma}{\partial y^\delta} + \Gamma_{\delta\gamma}^\sigma v^\gamma \right) \right) \\ & - \phi_2 g^{\alpha\sigma} \frac{\partial p}{\partial y^\sigma} = \sum_{k=1}^N z_k c_k g^{\alpha\sigma} \frac{\partial \psi}{\partial y^\sigma}. \end{aligned} \quad (5.59)$$

Given (5.32), the terms involving Christoffel symbols do not contribute to leading order in the inner layer. Using (5.27), we obtain:

$$\frac{\partial}{\partial \xi} \left( \frac{\partial v_f^{\alpha,0}}{\partial \xi} \right) = 0 \text{ for } \xi > 0. \quad (5.60)$$

A similar calculation for (5.39) yields:

$$\frac{\partial}{\partial \xi} \left( \eta_2 \frac{\partial v_2^{\alpha,0}}{\partial \xi} \right) = 0 \text{ for } \xi < 0. \quad (5.61)$$

The matching conditions are:

$$\begin{aligned} \lim_{\xi \rightarrow -\infty} v_2^{\alpha,0}(\mathbf{y}_\Gamma, \xi, t) &= \lim_{y^3 \rightarrow 0^-} v_2^{\alpha,0}(\mathbf{y}_\Gamma, y^3, t) \equiv v_{2,-}^{\alpha,0}, \\ \lim_{\xi \rightarrow \infty} v_f^{\alpha,0}(\mathbf{y}_\Gamma, \xi, t) &= \lim_{y^3 \rightarrow 0^+} v_f^{\alpha,0}(\mathbf{y}_\Gamma, y^3, t) \equiv v_{f,+}^{\alpha,0}. \end{aligned} \quad (5.62)$$

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

$$v_2^{\alpha,0}(\mathbf{y}_\Gamma, \xi, t) = v_{2,-}^{\alpha,0}(\mathbf{y}_\Gamma, t), \quad v_f^{\alpha,0}(\mathbf{y}_\Gamma, \xi, t) = v_{f,+}^{\alpha,0}(\mathbf{y}_\Gamma, t). \quad (5.63)$$

Consider the equation for  $\phi_2$  in (5.34). To leading order in the inner layer, we have, using (5.32):

$$-\hat{v}^{3,0} \frac{\partial \phi_2^0}{\partial \xi} + \frac{\partial (v_2^{3,0} \phi_2^0)}{\partial \xi} = 0. \quad (5.64)$$

Given the definition of  $\hat{\mathbf{v}}$  and (5.31), we have:

$$\hat{v}^{3,0} = v_1^{3,0} \Big|_{\xi=0^-}. \quad (5.65)$$

Using this and (5.63), (5.64) becomes:

$$\left( -v_1^{3,0} \Big|_{\xi=0^-} + v_2^{3,0} \Big|_{\xi=0^-} \right) \frac{\partial \phi_2^0}{\partial \xi} = 0. \quad (5.66)$$

By assumption (5.51), we conclude that  $\phi_2^0$  does not depend on  $\xi$ . Given  $\phi_1^0 + \phi_2^0 = 1$  from (5.34), we see that  $\phi_1^0$  is also independent of  $\xi$ . Using the usual matching conditions, we thus have:

$$\phi_i^0(\mathbf{y}_\Gamma, \xi, t) = \lim_{y^3 \rightarrow 0^-} \phi_i^0(\mathbf{y}_\Gamma, y^3, t) \equiv \phi_{i,-}^0. \quad (5.67)$$

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

$$\sum_{i=1}^2 \mathcal{D}_\sigma(\phi_i v_i^\sigma) = 0, \quad (5.68)$$

which can be obtained by summing the equations for  $\phi_i$  in (5.34) for  $i = 1, 2$ . To leading order, using (5.32), this equation yields:

$$\frac{\partial}{\partial \xi} (\phi_1^0 v_1^{3,0} + \phi_2^0 v_2^{3,0}) = 0 \text{ for } \xi < 0. \quad (5.69)$$

This shows that:

$$\phi_1^0 v_1^{3,0} + \phi_2^0 v_2^{3,0} = C_1 \quad (5.70)$$



where  $C_1$  does not depend on  $\xi$ . Since  $\phi_i^0$  and  $v_2^{3,0}$  are independent of  $\xi$ , so is  $v_1^{3,0}$ . The matching condition yields:

$$v_1^{3,0}(\mathbf{y}_\Gamma, \xi, t) = \lim_{y^3 \rightarrow 0^-} v_1^{3,0}(\mathbf{y}_\Gamma, y^3, t) \equiv v_{1,-}^{3,0}(\mathbf{y}_\Gamma, t). \quad (5.71)$$

We now examine equations (5.39) and (5.40). The leading order equation only allowed us to show that  $v_2^{\alpha,0}$  and  $v_f^{\alpha,0}$  were constant in  $\xi$ . To obtain (5.17), we must look at the next order in  $\beta$ . Let us first consider (5.40), or equivalently (5.59). After some calculation, using (5.32), (5.27), (5.29) and (5.62) we obtain:

$$2\zeta \frac{\partial}{\partial \xi} \left( \frac{\partial v_f^{3,1}}{\partial \xi} \right) - \frac{\partial p^0}{\partial \xi} = \sum_{k=1}^N z_k c_k^0 \frac{\partial \psi}{\partial \xi} \text{ for } \xi > 0. \quad (5.72)$$

A similar calculation using (5.39) yields:

$$2\zeta \frac{\partial}{\partial \xi} \left( \eta_2(\phi_{2,-}^0) \frac{\partial v_2^{3,1}}{\partial \xi} \right) - \phi_{2,-}^0 \frac{\partial p^0}{\partial \xi} = \sum_{k=1}^N \phi_{2,-}^0 z_k c_k^0 \frac{\partial \psi^0}{\partial \xi} \text{ for } \xi < 0, \quad (5.73)$$

where (5.67) was used to rewrite  $\phi_2^0$ . Using (5.57), the above two equations can be rewritten as follows:

$$\frac{\partial}{\partial \xi} \left( 2\zeta \frac{\eta_2(\phi_{2,-}^0)}{\phi_{2,-}^0} \frac{\partial v_2^{3,1}}{\partial \xi} - p^0 + \sum_{k=1}^N c_k^0 \right) = 0 \text{ for } \xi < 0, \quad (5.74)$$

$$\frac{\partial}{\partial \xi} \left( 2\zeta \frac{\partial v_f^{3,1}}{\partial \xi} - p^0 + \sum_{k=1}^N c_k^0 \right) = 0 \text{ for } \xi > 0, \quad (5.75)$$

where we also used the fact that  $\phi_{2,-}^0$  is independent of  $\xi$  (see (5.67)) in the first equality. At  $\xi = 0$ , we have the following condition from (5.41):

$$\eta_\perp(v_{f,+}^{3,0} - v_{1,-}^{3,0}) = p^0|_{\xi=0^-} - p^0|_{\xi=0^+} - 2\zeta \frac{\eta_2(\phi_{2,-}^0)}{\phi_{2,-}^0} \frac{\partial v_2^{3,1}}{\partial \xi} + 2\zeta \frac{\partial v_f^{3,1}}{\partial \xi} \quad (5.76)$$

where we used the definition of  $w$ , (5.63) and (5.71) to obtain the left hand side of the above relation. We also need the matching condition:

$$\lim_{\xi \rightarrow \pm\infty} p^0(\mathbf{y}_\Gamma, \xi, t) = \lim_{y^3 \rightarrow 0^\pm} p^0(\mathbf{y}_\Gamma, y^3, t) \equiv p_\pm^0. \quad (5.77)$$

Let us first consider the (5.75). We immediately have:

$$2\zeta \frac{\partial v_f^{3,1}}{\partial \xi} - p^0 + \sum_{k=1}^N c_k^0 = C_2 \quad (5.78)$$

where  $C_2$  does not depend on  $\xi$ . Using (5.56) and (5.77), we have:

$$\lim_{\xi \rightarrow \infty} 2\zeta \frac{\partial v_f^{3,1}}{\partial \xi} = C_2 + p_+^0 - \sum_{k=1}^N c_{k,+}^0. \quad (5.79)$$

By the l'Hôpital rule, we have:

$$\lim_{\xi \rightarrow \infty} \frac{v_f^{3,1}(\xi)}{\xi} = \frac{1}{2\zeta} \left( C_2 + p_+^0 - \sum_{k=1}^N c_{k,+}^0 \right) \equiv s_+. \quad (5.80)$$

Therefore, we have:

$$v_f^{3,1}(\mathbf{y}_\Gamma, \xi, t) = s_+(\mathbf{y}_\Gamma, t)\xi + r, \quad \lim_{\xi \rightarrow \infty} \frac{r}{\xi} = 0. \quad (5.81)$$

Writing out the inner solution for  $v_f^3$  to order  $\beta$ , we have:

$$v_f^3(\mathbf{y}_\Gamma, \xi, t) = v_{f,+}^{3,0}(\mathbf{y}_\Gamma, t) + \beta s_+(\mathbf{y}_\Gamma, t)\xi + \beta r(\mathbf{y}_\Gamma, \xi, t) + \dots \quad (5.82)$$

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

$$v_f^3(\mathbf{y}_\Gamma, y^3, t) = v_{f,+}^{3,0}(\mathbf{y}_\Gamma, y^3, t) + \beta v_f^{3,1}(\mathbf{y}_\Gamma, y^3, t) + \dots \quad (5.83)$$

We now invoke the Kaplun matching procedure [21, 27]. Introduce an intermediate coordinate system  $\eta$  such that:

$$\beta\xi = y^3 = \beta^\alpha \eta, \quad 0 < \alpha < 1. \quad (5.84)$$

The matching procedure is to write (5.82) and (5.83) in terms of  $\eta$  and require that like terms in  $\beta$  be identical. From (5.82), we have:

$$v_f^3(\mathbf{y}_\Gamma, \beta^{\alpha-1}\eta, t) = v_{f,+}^{3,0}(\mathbf{y}_\Gamma, t) + \beta^\alpha \eta s_+(\mathbf{y}_\Gamma, t) + \beta r(\mathbf{y}_\Gamma, \beta^{\alpha-1}\eta, t) + \dots \quad (5.85)$$

From (5.83), we have:

$$v_f^3(\mathbf{y}_\Gamma, \beta^\alpha \eta, t) = \lim_{y^3 \rightarrow 0^+} v_{f,+}^{3,0}(\mathbf{y}_\Gamma, y^3, t) + \beta^\alpha \eta \lim_{y^3 \rightarrow 0^+} \frac{\partial v_{f,+}^{3,0}}{\partial y^3}(\mathbf{y}_\Gamma, y^3, t) + \dots \quad (5.86)$$

Comparing the  $\beta^0$  term simply reproduces (5.62). Comparing the  $\beta^\alpha$  term yields:

$$\lim_{y^3 \rightarrow 0^+} \frac{\partial v_{f,+}^{3,0}}{\partial y^3}(\mathbf{y}_\Gamma, y^3, t) = s_+(\mathbf{y}_\Gamma, t). \quad (5.87)$$

We may perform a similar calculation on (5.75) to obtain:

$$\begin{aligned} \lim_{y^3 \rightarrow 0^-} \frac{\partial v_2^{3,0}}{\partial y^3}(\mathbf{y}_\Gamma, y^3, t) &= \frac{\phi_{2,-}}{2\zeta\eta_2(\phi_{2,-})} \left( C_3 + p_-^0 - \sum_{k=1}^N c_{k,-}^0 \right), \\ C_3 &= 2\zeta \frac{\eta_2(\phi_{2,-}^0)}{\phi_{2,-}^0} \frac{\partial v_2^{3,1}}{\partial \xi} - p^0 + \sum_{k=1}^N c_k^0. \end{aligned} \quad (5.88)$$

where  $C_3$  does not depend on  $\xi$ . Combining (5.76), (5.78), (5.80), (5.87) and (5.88), we have:

$$\begin{aligned} \eta_\perp (v_{f,+}^{3,0} - v_{1,-}^{3,0}) &= p_-^0 - p_+^0 - \sum_{k=1}^N c_{k,-}^0 + \sum_{k=1}^N c_{k,+}^0 \\ &\quad - \lim_{y^3 \rightarrow 0^-} 2\zeta \frac{\eta_2(\phi_2^0)}{\phi_2^0} \frac{\partial v_2^{3,0}}{\partial y^3} + \lim_{y^3 \rightarrow 0^+} 2\zeta \frac{\partial v_f^{3,0}}{\partial y^3}. \end{aligned} \quad (5.89)$$

This is nothing other than (5.17).

**6. Conclusion.** In this paper, we presented dynamic models of polyelectrolyte gels. In Section 3, we first presented a purely mechanical model of neutral gels. The equations satisfied in the bulk are not new. What is new here is the interface conditions at the moving gel-fluid interface. We discussed how previously proposed interface conditions can be obtained as limiting cases of the interface condition proposed in this paper.

In Section 4, we discussed how we can incorporate the electrodiffusion of ions to formulate a model of polyelectrolyte gels. We establish a free energy identity for this system. We believe this is the first dynamic model of polyelectrolyte gels immersed in fluid that satisfies this free energy dissipation principle.

In Section 5, we discuss the electroneutral limit. Here, we find that the Lorentz force at the gel-fluid interface gives rise to the van't Hoff expression for osmotic pressure in this limit. It is therefore physically inconsistent to use the Poisson equation and the van't Hoff expression for osmotic pressure at the same time in the context of polyelectrolyte gels, a practice that is seen in the literature.

We mention that there are models in which the ions are also treated to have a volume fraction, resulting in a multiphase rather than a biphasic continuum model [5, 6, 19, 20]. This is different from our approach, in which the ions are volume-less solutes dissolved in the solvent or fluid phase. It would be interesting to clarify the relationship between these two approaches.

The model presented here leaves out some effects that can be important in specific polyelectrolyte gel systems. One such effect is the binding and unbinding of ions to the network charges. In this paper, the ions diffuse into and out of the gel but never bind to the network. This effect can be very important for protons and for divalent cations such as calcium. Incorporation of protonation is likely straightforward, but the binding reactions for divalent cations may present some challenges, as they seem to act as bridging agents affecting the mechanical properties of the polymer network.

We also point out that the equations we have written down is a mean-field theory in which all physical quantities are macroscopic quantities. It would be of interest to see how these macroscopic equations are related to the underlying microscopic physics. This may lead to better macroscopic equations, or to multiscale systems, applications of which have been successful, for example, in the dynamics of polymeric fluids [33, 50]. Such considerations may also suggest physically appropriate regularizations of the incompressibility condition (2.3), a strict imposition of which may pose analytical and computational difficulties.

In subsequent work, we hope to use our model to study the dynamics of polyelectrolyte gels and their application in artificial devices [10, 35]. Both the analysis of and numerical computation with our equations will be aided by the presence of the free energy identity.

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