### Introduction

Gels are crosslinked three dimensional polymer networks that absorb solvent and swell without dissolu-  $\frac{1}{2}$ tion. Polyelectrolyte gels carry fixed charge groups.  $\stackrel{\smile}{\simeq}$ Many polyelectrolyte gels experience volume phase transition due to small changes in various environmental parameters such as pH or temperature. The 530volume phase transition is widely used in artificial devices.



Goal: to understand volume phase transition of polyelectrolyte gels.

#### **Equations for the Model**

Let gel occupy region  $\Omega_t \subset \mathbb{R}^3$ , surrounded by fluid  $\mathcal{R}_t$ . The medium has two phases: phase 1 as polymer and phase 2 as fluid. In  $\Omega_t$ , let  $\phi_i$ ,  $\mathbf{v}_i$  be volume fractions and velocities, respectively. They satisfy

$$\phi_1 + \phi_2 = 1, \quad \frac{\partial \phi_i}{\partial t} + \nabla \cdot (\mathbf{v}_i \phi_i) = 0, \quad i = 1, 2$$

hence the mixture is incompressible:

 $\nabla \cdot (\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) = 0.$ The force balance equations for polymer and fluid are

$$\nabla \cdot \mathcal{T}_{i} - \phi_{i} \nabla p + \mathbf{f}_{i} = 0, \quad i = 1, 2;$$
  
$$\mathcal{T}_{1} = \mathcal{T}_{1}^{FH} + \mathcal{T}_{1}^{elas} + \mathcal{T}_{1}^{visc}, \quad \mathcal{T}_{2} = \mathcal{T}_{2}^{visc}, \quad \mathcal{T}_{i}^{visc} = \frac{1}{2} \eta_{i} (\nabla \mathbf{v}_{i} + \nabla \mathbf{v}_{i})$$
  
$$\mathbf{f}_{1} = \mathbf{f}_{fric} - \phi_{1} \rho_{p} \nabla \psi, \quad \mathbf{f}_{2} = -\mathbf{f}_{fric} - \sum_{k=1}^{N} q z_{k} \phi_{2} c_{k} \nabla \psi, \quad \mathbf{f}_{fric} = \kappa (\mathbf{v}_{2} + \mathbf{v}_{1})$$

The ionic concentrations  $c_k$  satisfy electro-diffusion equations under neutrality constraint:

in which  $D_k$ : diffusion coefficient,  $z_k$ : valence of ion,  $\psi$ : electrostatic potential,  $\rho_p$ : fixed charge density on polymer,  $\mu_k$ : chemical potential.

We assume in the outside fluid  $\mathcal{R}_t$ , the velocity field satisfies the Stokes equation, and ionic concentrations satisfy electro-diffusion equations under the electro-neutrality constraint.

### **Boundary conditions at the interface**

The polymer has mass balance in normal and tangential directions:

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

For ionic concentrations, the flux is continuous:

$$\left( (\mathbf{v}_f - \mathbf{v}_1)c_k - \frac{D_k c_k}{k_B T} \nabla \mu_k \right) \cdot \mathbf{n} |_{\mathcal{R}_t} = \left( (\mathbf{v}_2 - \mathbf{v}_1)\phi_2 c_k - \frac{D_k c_k}{k_B T} \nabla \mu_k \right)$$

Force balance of total stress, normal fluid stress and tangential fluid stress:

$$\mathcal{T}_{f}\mathbf{n} - (\mathcal{T}_{1} + \mathcal{T}_{2})\mathbf{n} + [p]\mathbf{n} = 0, \quad [p] = p|_{in} - p|_{out},$$
$$\eta_{\perp}w = \mathbf{n} \cdot (\mathcal{T}_{f}\mathbf{n}) - \mathbf{n} \cdot \phi_{2}^{-1}(\mathcal{T}_{2}\mathbf{n}) + [p] - \pi_{osm}, \quad \pi_{osm} = k_{B}T\sum_{k=1}^{N} (\mathcal{T}_{f}\mathbf{n} - \mathcal{T}_{2}\mathbf{n})_{\parallel} = \eta_{\parallel}\mathbf{q}.$$

At outside boundary  $\partial \mathbb{U}$ , we assume the domain does not move, and ion flux is zero:

$$\mathbf{v}_f = 0, \quad (\mathbf{v}_f c_k - \frac{D_k c_k}{k_B T} \nabla \mu_k) \cdot \mathbf{n} = 0.$$

A Dynamic Model of Polyelectrolyte Gels HAORAN CHEN, YOICHIRO MORI, MARIA-CARME CALDERER

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 $c_k = 0$ 

 $\equiv$  q.

 $\cdot \mathbf{n}|_{\Omega_t}$ .

 $[c_k],$ 

## **Energy Dissipation Identity**

We have the following free energy dissipation identity:

$$\begin{aligned} \frac{d}{dt}(E_{elas} + E_{FH} + E_{ion}) &= -I_{visc} - I_{diff} - J_{visc}, \\ E_{elas} &= \int_{\Omega_t} \phi_1 \mathcal{W}_{elas}(\mathcal{F}) d\mathbf{x}, \quad E_{FH} = \int_{\Omega_t} \mathcal{W}_{FH}(\phi_1) d\mathbf{x}, \\ E_{ion} &= \int_{\Omega_t} \left( \phi_2 \sum_{k=1}^N c_k \ln c_k \right) d\mathbf{x} + \int_{\mathcal{R}_t} \left( \sum_{k=1}^N c_k \ln c_k \right) d\mathbf{x}, \\ I_{visc} &= \int_{\Omega_t} \left( \sum_{i=1}^2 2\eta_i \, \|\nabla_S \mathbf{v}_i\|^2 + \kappa \, |\mathbf{v}_1 - \mathbf{v}_2|^2 \right) d\mathbf{x} + \int_{\mathcal{R}_t} 2\eta_f \, \|\nabla_S \mathbf{v}_f\|^2 \, d\mathbf{x}, \\ I_{diff} &= \int_{\mathbb{U}} \frac{D_k c_k}{k_B T} \, |\nabla \mu_k|^2 \, d\mathbf{x}, \quad J_{visc} = \int_{\Gamma_t} \left( \eta_\perp w^2 + \eta_\parallel |\mathbf{q}|^2 \right) dS. \end{aligned}$$

The equations and boundary conditions can be derived from the above energy identity via the Onsager variational principle.

## Linear Stability Analysis, 1-D case

#### **Steady State Solution**

solution satisfies

We assume the free energy  $f(\phi_1)$  is convex. For gels with no ion species, the unique steady state  $\phi_1 \equiv \phi_0, \quad f(\phi_0) - \phi_0 f'(\phi_0) = 0.$ 

For polyelectrolyte gels, the unique steady state solution  $\phi_1 \equiv \phi_0$  is implicitly determined by initial data such as total ion concentrations and gel volume.

#### **Nonionic Decay Rate**

In 1-D case, let  $\mathbb{U} = (0, L)$  and l < L be gel length, and  $\epsilon u(X, t)$  be a small perturbation near the steady state. Then u(X, t) follows

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

with certain boundary condition at the two interfaces. When the gel is fully permeable, namely  $\eta_{\perp} = 0,$ 9 ....

$$\lambda_j = A_j(l) := \frac{\phi_0^2 f''(\phi_0)}{\frac{4\kappa l^2}{(1-\phi_0)^2 j^2 \pi^2} + H}$$

A similar analysis can be performed when  $\eta_{\perp} \neq 0$ . Note that  $A_i$  are determined only by mechanical properties of the gel.

### **Ionic Decay Rate, fast diffusive surrounding fluid**

In 1-D case, when  $\mathbb{U} = \Omega_t = (0, L)$ , eigenvalues satisfy

$$\frac{\alpha_p}{\lambda - A_j(L)} + \sum_{k=1}^N \frac{\alpha_k}{\lambda - B_{k,j}(L)} = 0$$
(1)

in which

$$B_{k,j}(L) = \frac{D_k j^2 \pi^2}{(1-\phi_0)L^2}, \quad \alpha_p \propto \rho_p^2, \quad \alpha_k \propto \frac{D_k}{1-\phi_0} z_k^2 \exp(-z_k \psi)$$

Here,  $B_{i,j}$  can be considered as intrinsic spectrum of an ion species, which dissolves in the fluid of gel region. In particular, the principal  $\lambda$  lies between the smallest and the second smallest  $\{A_j, B_{k,j}\}.$ 

#### **Decay rate change as gel being charged**

Equation (1) enables us to find the trend of  $\lambda$  as  $\rho_p$  changes. Fix the concentrations of ions in the surrounding fluid and charge the gel, there are three possibilities: (i) if  $A_1 < B_{k,j}$  for all  $k, \frac{d\lambda_1}{d\rho_n}$  is uncertain;

(ii) otherwise,  $B_{k_0,1}$  is the smallest, and if N = 2, we have  $\operatorname{sgn}(\frac{d\lambda_1}{d\rho_n}) = \operatorname{sgn}(-z_{k_0})$ ; (iii) in (ii), N > 2, the conclusion is likely in many situations, but uncertain in general.

for  $j \in \mathbb{N}$ 

#### Ionic Decay Rate, two ion species, one side

We consider a 1-D case with

- Let  $\lambda$  be the principal eigenvalue. It follows

$$\lambda < \min\left\{B_{1,\frac{3}{2}}(a), B_{2,\frac{3}{2}}(a), \frac{D_{out}}{(L-a)^2}\right\}, D_{out} = \frac{(|z_1| + |z_2|)D_1D_2}{|z_1|D_1 + |z_2|D_2};$$

$$\lambda > \min\left\{A_1(a), \ \frac{\pi^2}{4} \cdot \frac{D_{out}}{1-\phi}\right\}.$$

the lower bound estimate can be applied to the general case or not.

# Numerical Simulations of 1-D polyelectrolyte gel

The force balance equation in  $\Omega_t$  is discretized in the reference configuration. We use the backward Euler method for time discretization. At t = 0, the values of the electrostatic potential and the velocity of gel are implicit, they are calculated by iteration along a homotopy path from the solved steady state solution. The following is an example showing  $\phi_1$ ,  $c_1$ ,  $c_2$  and  $\psi$  at t = 0, 0.1, 1, 10.



## **Ongoing & Future work**

- We will simulate 2-D or 3-D spherical case with/without ion species.

### References

Y. Mori, H. Chen, C. Micek and M.C. Calderer, A dynamic model of polyelectrolyte gels, 2012, SIAM Journal of Applied Mathematics, accepted. H. Chen, Y. Mori, Model development and simulation of polyelectrolyte gels, in preparation.



(1)  $\Omega_t = (0, a), \quad \mathcal{R}_t = (a, L), \quad a = a(t);$ (2) there are two ion species, *i.e.* N = 2; (3) the gel is fully permeable, *i.e.*  $\eta_{\perp} = 0$ .

• An upper bound estimate of  $\lambda$  holds for any situation:

• An lower bound estimate of  $\lambda$  holds if  $|z_1| < |z_2|$  and  $A_1(a) < \frac{D_1}{1-\phi} < \frac{D_2}{1-\phi}$ :

• The behavior of  $\lambda$  with respect to changing value of  $D_k$  is not clear, so it is not obvious whether

• We will consider nonconvex energy and study phase separation phenomena.