A Dynamic Model of Polyelectrolyte Gels
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Introduction

Gels are crosslinked three-dimensional polymer networks that absorb solvent and swell without dissolution. Polyelectrolyte gels carry fixed charge groups. Many polyelectrolyte gels experience volume phase transition due to small changes in various environmental parameters such as pH or temperature. The volume 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 $\Omega \subset \mathbb{R}^2$, surrounded by fluid $\mathcal{K}_1$, $\mathcal{K}_2$. The medium has two phases: phase 1 as polymer and phase 2 as fluid. In $\Omega$, let $\phi_j$, $v_j$ be volume fractions and velocities, respectively. They satisfy

$$\phi_1 + \phi_2 = 1, \quad \frac{\partial \phi_j}{\partial t} + \nabla \cdot (\phi_j v_j) = 0, \quad i, j = 1, 2$$

hence the mixture is incompressible: $\nabla \cdot (\phi_1 v_1 + \phi_2 v_2) = 0$.

The force balance equations for polymer and fluid are

$$\nabla \cdot \mathbf{f}_j + \phi_j \rho_j \mathbf{g} + \mathbf{f}_j = 0, \quad i, j = 1, 2$$

with

$$\mathbf{f}_1 = \nabla \cdot \mathbf{f}_1, \quad \mathbf{f}_2 = -\nabla \cdot \mathbf{f}_2 - \frac{N}{\xi^2} \phi_2 \rho_2 \mathbf{f}_2 (\nabla \phi_2 - \nabla \phi_1)$$

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

$$\nabla \cdot (\phi_1 \psi c_k \nabla \psi) + \nabla \cdot (\phi_2 \psi c_k \nabla \psi) = 0$$

in which $D_k$ is the diffusion coefficient, $q_k$ is the charge, $\psi$ is the electrostatic potential, $\rho_k$ is the fixed charge density on polymer, $\mu_k$ is the chemical potential.

We assume in the outside fluid $\mathcal{K}_2$, the velocity field satisfies the Stokes equation, and ion 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:

$$(\psi - \psi_j) \cdot n = 0$$

For ion concentrations, the flux is continuous:

$$\left( \frac{\partial (\psi - \psi_j)}{\partial t} - \frac{\bar{D}_j c_j}{\bar{D}_j c_j} \nabla \psi \right) \cdot n = 0$$

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

$$\mathbf{T}_j = (\mathbf{T}_j^N + \mathbf{T}_j^T)(n) \cdot n = 0, \quad \mathbf{T}_j^T = \mathbf{T}_j^T(n) \cdot \eta_j \mathbb{I}$$

At outside boundary $\mathcal{K}_2$, we assume the domain does not move, and ion flux is zero:

$$\psi_j = 0, \quad (\psi_j - \phi_j \psi c_k \nabla \psi) \cdot n = 0$$

Energy Dissipation Identity

We have the following free energy dissipation identity:

$$\frac{d}{dt} \psi (\mathbf{f}_j^N + \mathbf{f}_j^T) + E_{\mathcal{K}_j} = -E_{\mathcal{K}_j} + I_{\mathcal{K}_j}$$

with

$$E_{\mathcal{K}_j} = \int (\phi_j \psi c_k \mathbf{f}_j^N \cdot \nabla \psi - \phi_j \psi c_k \mathbf{f}_j^T \cdot \nabla \psi) \, dV$$

$$I_{\mathcal{K}_j} = \int \left( \sum_{k=1}^{N} -2 \nabla \psi \cdot \nabla (\phi_j \psi c_k \mathbf{f}_j^N) \right) \, dV$$

Boundary conditions at the interface

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

Linear Stability Analysis, 1-D case

Steady State Solution

We assume the free energy $f(\phi_j)$ is convex. For gels with no ion species, the unique steady state solution satisfies

$$\phi_1 = \phi^*_1, \quad f(\phi_1) = f(\phi^*_1) = 0$$

For polyelectrolyte gels, the unique steady state solution $\phi_1 \equiv \phi_2$ is implicitly determined by initial data since total ion concentrations and gel volume. $\phi_j$ is the chemical potential of the gel.

Nonionic Decay Rate

In 1-D case, let $U = (U^0, L)$, and $L$ be gel length, and we fix $X$ to be a small perturbation near the steady state. Then $u_j(X, t)$ follows

$$Hu_{1j} + \frac{\partial \phi_j c_j^0 u_j}{\partial t} = -\phi_j \frac{\partial f_{j1}}{\partial \phi_j} \psi c_k \mathbf{f}_j^N \cdot \nabla \psi = 0$$

with certain boundary condition at the two interfaces. When the gel is fully permeable, namely $\eta_2 = 0$,$\eta_1 = 0$,

$$\lambda_j = \lambda_j(X) = \frac{\partial \phi_j c_j^0 u_j}{\partial t}$$

for $j \in N$

A similar analysis can be performed when $\eta_1 \neq 0$. Note that $\lambda_j$ are determined only by mechanical properties of the gel.

Ionic Decay Rate, fast diffusive surrounding fluid

In 1-D case, we have $U = (0, L)$, eigenvalues satisfy

$$\left( \phi_j \lambda^2 - \frac{\partial \phi_j c_j^0 u_j}{\partial t} \right) \sum_{k=1}^{N} \frac{\partial \phi_j c_j^0 u_j}{\partial \phi_j} \psi c_k \mathbf{f}_j^N \cdot \nabla \psi_{j-k} + \sum_{k=1}^{N} \frac{\partial \phi_j c_j^0 u_j}{\partial \phi_j} \psi c_k \mathbf{f}_j^N \cdot \nabla \psi_{j-k} = 0$$

in which

$$\frac{\partial \phi_j c_j^0 u_j}{\partial t} = \frac{\partial \phi_j c_j^0 u_j}{\partial t} + \frac{\partial \phi_j c_j^0 u_j}{\partial t} \psi c_k \mathbf{f}_j^N \cdot \nabla \psi_{j-k}$$

Here, $R_{j-k}$ can be considered as intrinsic spectrum of an ion species, which depends on the fluid of gel region. In particular, the principal $\lambda$ lies between the smallest and the second smallest ($\lambda_j, \lambda_{j-k}$).

Decay rate change as gel being charged

Equation (1) enables us to find the trend of $\lambda$ as $\rho_j$ changes. Fix the concentrations of ions in the surrounding fluid and change the gel, there are three possibilities:

(i) if $\lambda_j > 0$ for all $k$, $\frac{\partial \phi_j c_j^0 u_j}{\partial t}$ is uncertain;

(ii) otherwise, $\lambda_{j-k}$ is the smallest, and if $N = 2$, we have $\frac{\partial \phi_j c_j^0 u_j}{\partial t} \approx \phi_j \frac{\partial f_{j1}}{\partial \phi_j} \psi c_k \mathbf{f}_j^N \cdot \nabla \psi$;

(iii) in (ii), $N > 2$, the conclusion is likely in many situations, but uncertain in general.

Ionic Decay Rate, two ion species, one side

We consider a 1-D case with

$$(1) \quad \eta_2 = 0, \quad \eta_1 = \alpha(\bar{L})$$

$$(2) \quad \eta_1 = 0, \quad \eta_2 = \alpha(\bar{L})$$

there are two ion species, $i = 0, 1$, the gel is fully permeable, i.e. $\eta_2 = 0$.

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

- An upper bound estimate of $\lambda$ holds for any side:

$$\lambda \leq \min \{ \alpha(\bar{L}) \}$$

- An lower bound estimate of $\lambda$ holds if $|z_1| > |z_2|$ and $\alpha(\bar{L}) < \alpha_1 \leq \alpha_2$:

$$\lambda > \min \{ \alpha_1(\bar{L}) \}$$

- The behavior of $\lambda$ with respect to changing value of $\eta_2$, $\eta_1$ is not clear, so it is not obvious whether 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 $\Omega$ 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 interpolation 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 $t = 0, 0.1, 1, 10$

$\phi_1 = 0.5, \phi_2 = 0.5, \psi_1 = 0, \psi_2 = 0$.

$$f(\phi) = \frac{1}{2} (1 - \phi)^2 \quad \lambda = 5, \quad a = \beta = \lambda = 0.5$$

$c_1(t = 0) = 2.09 \pm 0.05 \times x$ for $0 < x < 3$;

$c_1(t = 0) = 2.07 \pm 0.05 \times 5$ for $3 < x < 5$.

The linear approximations of $\lambda_0, \lambda_1, \lambda_2$ match with the theoretical value.

Ongoing & Future work

- We will consider nonconvex energy and study phase separation phenomena.
- We will simulate 2-D or 3-D spherical case with/without ion species.

References
