

**A Thermomechanical Model of Gels**

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# Dedication

To my husband, Jaebeom and my sister, Yeon-Kyoung.

## Abstract

In this thesis, a model of polymer gels on thermal effects is developed and analyzed, and numerical simulations for a one-dimensional geometry is performed. Gels are useful materials in many manufacturing as well as biomedicine, by use of which a variety of apparatus such as drug delivery devices are designed. It is important in physics to observe how gels change under different temperature, and in particular, we examine how gels respond to the gradient of temperature. Even though temperature is a key factor to be considered, no physical theory with thermal gradients has been presented. That becomes a motivation for this work, and we construct a thermodynamic theory of gels and apply it to investigate several phenomena in the one-dimensional geometry, such as the evolution of the interface between the gel and the environmental fluid.

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# Chapter 1

## Introduction

Gels are cross-linked polymer networks immersed but not dissolved in a solvent. The cross-links in polymer networks cause solid-like behavior of gels, but addition of solvent helps gels to become softer and swollen by degrees. Gels present itself in nature in animal and plant tissues. Gels are also found in a wide range of applications from foods to many manufacturing devices like contact lenses, hair gel and paints, to medical devices such as drug delivery devices or implants.

In this thesis, we develop and analyze a model of polymer gels driven by thermal effects. We have incorporated thermal effects into the equations of gel dynamics. This is particularly relevant for implanted biomedical devices. After the device is implanted into the body, it should adapt to the body environment to work stably in the body. One of the factors that influence the device is temperature, and it is important to consider how the device responds to temperature change. Mathematical modeling and analysis of thermodynamics of gels is thus significant to the biomedicine. Nonetheless, no physical theory for such system was available. That becomes a motivation for this work, and we take this system into account and develop thermal effects on it.

We assume that the gel is non-ionic, immiscible, and incompressible. Due to the assumption of *non-ionic* gel, electrical effects can be neglected. The *immiscibility* means that the responses in the mixture are depending on volume fractions. On the contrary to this, we call a mixture miscible if corresponding constitutive equations are independent of the volume fractions. Similarly, the *incompressibility* characterizes a mixture as follows. For a single body, an incompressible one is referred to a body in which its

divergence of velocity is free. Mass balance yields zero material time derivative of density, that is, the mass density is constant. In the case of a mixture, we distinguish two kinds of densities, the bulk density and the intrinsic (*or* true) density for each component.  $\rho_i$  denotes the bulk density of the  $i$ th component which stands for the mass of the  $i$ th constituent per unit volume of mixture. On the other hand, the intrinsic density of the  $i$ th component denoted by  $\gamma_i$  is its mass per unit true volume which the  $i$ th constituent occupies by itself. These two densities are intimately related by the volume fraction  $\phi_i$  as  $\rho_i = \gamma_i\phi_i$ , ( $i = 1, 2$ ). The mixture is said to be incompressible if the intrinsic density is independent of time for each constituent in the mixture. For convenience sake, in this paper, we identically set the intrinsic densities to be one, and deal with volume fractions for polymer and solvent in the gel instead of bulk densities. In addition, we assume that inertial effects are neglected in the system to characterize its slow motion.

The incompressibility assumption on the mixture is mathematically set as each of the components having constant mass density when found in the single phase. This, together with the saturation assumption, that is  $\phi_1 + \phi_2 = 1$ , gives the relation  $\nabla \cdot (\mathbf{v}_1\phi_1 + \mathbf{v}_2\phi_2) = 0$ . (We point out that, in some gel literature, this is known as the incompressibility condition of the mixture). Here,  $\mathbf{v}_i$  represents the velocity field of the individual components.

We postulate laws of balance of mass and linear momentum for each of the components, and the law of balance of energy for the whole system. Under constant temperature, the free energy density  $\psi$  of the gel, which characterizes the mechanical behavior, is often assumed to consist of two energy functions, the stored elastic energy function of the polymer network and the Flory-Huggins energy of mixing. However, inclusion of thermal energy is necessary when temperature is not constant. Since thermal effects are present, the internal energy density  $\varepsilon$  is also taken into consideration in order to account for the non-recoverable part of the energy due to heat and temperature as well as for the mechanical contribution. The thermodynamic relation  $\varepsilon = \psi + \theta\eta$ , where  $\theta > 0$  denotes absolute temperature, defines the entropy density( $\eta$ ) of the system.

The remaining constitutive equations include the stress tensor of each component, consisting of the sum of elastic and viscous parts, the pressure, the heat flux vector, and the drag forces between fluid and solid in the gel. Pressure is introduced as a Lagrange

multiplier associated with the incompressibility assumption on the mixture.

We assume that the system, comprising the gel and the surrounding fluid, is thermally isolated. The Second Law of Thermodynamics states that the total entropy is non-decreasing in such a thermally insulated system. We follow the procedure developed in [1] and found as well in [2] and [3] that uses the Second Law of Thermodynamics to derive restrictions on the constitutive equations of the material. We point out that the approach to derive the constitutive equations is not a trivial generalization of the case with a single phase. In particular, it takes special care to define the total internal energy density of the mixture. The approach presented here is different from previous works on multi-component mixtures with thermal effects [5], [6] which define the total energy as the sum of energies of components in the mixture. Indeed, measuring the energy values of each constituent separately is almost impossible. Instead, the total energy of mixture is given as a whole in most cases. For this reason, in this thesis, we take a different point of view for the description of energy. It is, in fact, the other way around. Given representation of free energy density per unit volume for the whole mixture, we derive both the internal energy density and entropy density for the gel from thermodynamic relations, and at the same time those quantities associated with the individual components are derived by the thermodynamic property of energy that the energy function be “extensive”.

In the system concerned here, the gel is entirely submerged in its own fluid without touching the boundary of the system and fluid moves through the gel freely. This is a special feature of the gel model presented here; the boundary conditions follow from postulating balance laws across the interface between the gel and its surrounding fluid. This approach was first developed in [23], for the purely mechanical case as well as the case when families of ions are present in the system. In all such situations, the problem becomes a system of partial differential equations with a free boundary that being the interface between gel and fluid, assumed to move with the normal component of the polymer velocity at that boundary.

Before giving the outline of this dissertation, we summarize some related results concerning mixture theory. The classical book [4] deals extensively with mathematical models of mixture theories, in abstract physical frameworks. Although such a reference is an outstanding resource to assist on the studies of mixture theories, none of the

models there was directly relevant to our problems. The paper [23], on the dynamics of polyelectrolyte gels, without including thermal effects, starts with postulating mechanical equations for each component as well as the balance of energy of the system. Proper boundary conditions at the interface between the gel and the outer fluid are postulated, as well as the diffusion equations of ion species. Then dissipation laws of the energy that include the Flory-Huggins mixing energy, the polymer elastic energy and the ionic and electrostatic energies are shown. These give rise to a governing system of equations that it is subsequently studied in the one dimensional case. A mathematical model of dynamics of gels is studied by B. Chabaud and M. C. Calderer ([18]), with focus on the immiscible and incompressible gel mechanics, neglecting ionic and thermal effects. The article analyzes well-posedness of the coupled inertialess elasticity-Stokes problem, with boundary conditions ranging from impermeable to fully permeable. In this article, residual stresses are taken into account, which poses a challenge to the linear stability analysis. Further, they consider two different kinds of solvent type: inviscid and viscous. In [6], Dunwoody states basic balance equations for a mixture that consists of constituents more than two with different temperature postulating a general entropy inequality. Such governing equations are subsequently applied to a binary solid-fluid mixture at a single temperature under the assumption that there are no chemical reactions between components. However, a significant difference with the present approach is in that they postulate the equation of balance of energy for the gel, assuming that its boundary moves with the average velocity of the components. However, this does not seem to be a correct assumption for the present model, in part because the gel boundary is defined to be exactly the polymer boundary, and so it does move with the polymer velocity. Kenyon, in [7], concerns a mixture of  $N$ -fluid like constituents and a porous, deformable solid ( $N \geq 1$ ) having the same absolute temperature. In the article, chemical reactions are excluded, which results in zero growth of mass of each species. Balance equations and constitutive theory are also obtained by following the approach by Coleman & Noll. Finally, the equilibrium results are discussed, as usual. In [11], an application of the mixture theory to a two-phase flow is presented. The speed of boundary evolution is assumed to be that of either one of the two fluids, and so, it is also different from the assumption in the present work.

This thesis has the following organization. Chapter 2 provides a brief review of

fundamental principles of Continuum Mechanics and basic laws of Thermodynamics. In section 2.1, equations of mass conservation and balance of linear momentum for a single component elastic matter are presented. Section 2.2 discusses the equation of balance of energy and illustrates the procedure of derivation of constitutive equations and dissipation inequalities from the Second Law of Thermodynamics.

Chapter 3 describes the system under consideration and presents a mechanical model of the gel as well as conditions for the interface between the gel and the surrounding fluid.

In Chapter 4, we study the thermodynamics of gels. Based upon the first and the second laws of thermodynamics, in particular, section 4.1 and section 4.2 establish energy conservation equations and additional boundary conditions in the system. Section 4.3 presents a splitting of the energy of the whole gel into energies of the individual elements, for which the extensive property of energy is used, and in consequence, derives time-dependent equations for temperatures. Thermodynamics constitutive restrictions are obtained in section 4.4. Lastly, section 4.5 proves that the resulting equations for our system are invariant in Galilean relativity. The outcome of this chapter is the formulation of the initial boundary value problem for the evolution of the gel in an arbitrary domain submerged into the fluid.

Chapter 5 contains the governing equations of the gel in one dimensional geometry and a numerical scheme for solving the system. Section 5.1 provides the equations in one spatial dimension, and they are expressed in the referential forms in section 5.2. Subsequently, a numerical algorithm is proposed and convergence studies are carried out in section 5.3.

Chapter 6 demonstrates computational results. In section 6.1, we determine relatively crucial parameters in the motion of the gel on thermal effects by nondimensionalization of the governing equations. In section 6.2, we investigate conditions under which boundaries of the gel moves in the same direction by analytical computations together with numerical simulations.

Chapter 7, the final chapter of this thesis, presents conclusion as well as a summary of the work.

## Chapter 2

# Preliminaries

This chapter gives a review of basic laws in continuum mechanics and thermodynamics.

### 2.1 Basic Principles of Continuum Mechanics

We introduce some of the concepts used in this dissertation for the case of a single elastic material, occupying a bounded reference domain  $\Omega \subset \mathbb{R}^3$ , with smooth boundary  $\partial\Omega$ .

Let  $\Omega_t$  be the image of  $\Omega$  under the time-dependent *deformation map*  $\mathbf{x} = \boldsymbol{\varphi}(X, t)$ ,  $X \in \Omega$ . The *deformation gradient* is denoted by

$$F = \nabla \boldsymbol{\varphi}(\mathbf{X}, t),$$

and we assume that  $F$  is continuous and it satisfies the invertibility condition,  $\det F > 0$ .

**Remark.** Given the invertibility assumption on the deformation map, either material or spatial representations of a function,  $g(\mathbf{x}, t) = g(\boldsymbol{\varphi}(X, t), t) = G(X, t)$ , is considered as needed.

Let  $\mathcal{B} \subset \Omega$  denote any sub-body of the body, and  $\mathcal{B}_t$  the deformed body. We write  $\rho = \rho(\mathbf{x}, t)$  for the *mass density* at the spatial point  $\mathbf{x}$  in the current configuration. The

balance equations of mass and linear momentum are then the following:

$$\begin{aligned}\frac{d}{dt} \int_{\mathcal{B}_t} \rho(\mathbf{x}, t) d\mathbf{x} &= - \int_{\partial\mathcal{B}_t} \rho \mathbf{v} \cdot \mathbf{n} dA, \\ \frac{d}{dt} \int_{\mathcal{B}_t} \rho(\mathbf{x}, t) \mathbf{v}(\mathbf{x}, t) d\mathbf{x} &= - \int_{\partial\mathcal{B}_t} \rho \mathbf{v} (\mathbf{v} \cdot \mathbf{n}) dA + \int_{\partial\mathcal{B}_t} T \cdot \mathbf{n} dA + \int_{\mathcal{B}_t} \mathbf{b} d\mathbf{x},\end{aligned}$$

where  $\mathbf{n}$  denotes the outward unit normal vector from the boundary,  $\mathbf{v}$  the velocity field,  $T$  the Cauchy stress tensor,  $\mathbf{b}$  the body force, and  $\partial\mathcal{B}_t$  represents the boundary of  $\mathcal{B}_t$ . Since  $\mathcal{B}_t$  is arbitrary, we can formally express the previous balance equations in the local form

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (2.1)$$

$$\rho \left( \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right) = \nabla \cdot T + \mathbf{b}. \quad (2.2)$$

## 2.2 Basic Laws of Thermodynamics

This section provides the first two laws of thermodynamics and constitutive restrictions. The first law of thermodynamics is a statement of energy conservation and the second law states nonnegative production of entropy in a thermodynamic system. Here, we follow the approaches developed in [3] and [2] on the original work on reduction of constitutive equations by means of the Second Law of Thermodynamics [1].

We associate with each dynamical process the *specific internal energy*  $\varepsilon = \varepsilon(\mathbf{x}, t)$ , the *specific entropy*  $\eta = \eta(\mathbf{x}, t)$  and the *specific free energy*  $\psi = \psi(\mathbf{x}, t)$ . The net internal energy and entropy of  $\mathcal{B}_t$ , respectively, are given by

$$E(\mathcal{B}_t) = \int_{\mathcal{B}_t} \rho \varepsilon(\mathbf{x}, t) d\mathbf{x}, \quad S(\mathcal{B}_t) = \int_{\mathcal{B}_t} \rho \eta(\mathbf{x}, t) d\mathbf{x}.$$

**Note.** The term “*specific*” indicates the one measured per unit mass.

The heat entering the part  $\mathcal{B}_t$  per unit time is defined as

$$Q = - \int_{\partial\mathcal{B}_t} \mathbf{q} \cdot \mathbf{n} dA + \int_{\mathcal{B}_t} \rho r d\mathbf{x},$$



where  $\mathbf{q}$  denotes the *heat flux* vector and  $r$  the heat supply density (heat per unit mass entering the body per unit time).

The equation of energy balance is then

$$\frac{d}{dt} \int_{\mathcal{B}_t} \rho \varepsilon \, d\mathbf{x} = - \int_{\partial \mathcal{B}_t} (\varepsilon \rho \mathbf{v} + \mathbf{q}) \cdot \mathbf{n} \, dA + \int_{\partial \mathcal{B}_t} T \mathbf{v} \cdot \mathbf{n} \, dA + \int_{\mathcal{B}_t} \rho r \, d\mathbf{x},$$

and the arbitrariness of  $\mathcal{B}_t$  together with absence of heat supply leads to the local form

$$\rho \left( \frac{\partial \varepsilon}{\partial t} + (\mathbf{v} \cdot \nabla) \varepsilon \right) = T : \nabla \mathbf{v} - \nabla \cdot \mathbf{q}. \quad (2.3)$$

Now let us denote the *material time derivative* of a function with a superimposed *dot*. That is,

$$\dot{f}(x, t) := \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x} \frac{dx}{dt}.$$

The production of entropy per unit time in the part  $\mathcal{B}_t$  is defined by

$$\Gamma := \dot{S} + \int_{\partial \mathcal{B}_t} \frac{\mathbf{q}}{\theta} \cdot \mathbf{n} \, dA - \int_{\mathcal{B}_t} \frac{\rho r}{\theta} \, d\mathbf{x}. \quad (2.4)$$

The *Second Law of Thermodynamics* states that

$$\Gamma \geq 0,$$

for all  $\mathcal{B}_t \subset \Omega_t$ . The local form of this inequality, combined with equations ((2.1))-((2.3)) and Reynolds' transport theorem, becomes

$$\rho(\theta \dot{\eta} - \dot{\varepsilon}) + T : D - \frac{1}{\theta} \mathbf{q} \cdot \nabla \theta \geq 0, \quad (2.5)$$

where  $D = \frac{1}{2}(\nabla \mathbf{v} + \nabla \mathbf{v}^T)$ .

The following constitutive equations define a *thermoelastic material*:

$$T = T(\theta, \mathbf{g}, F, \dot{F}),$$

$$\eta = \eta(\theta, \mathbf{g}, F, \dot{F}),$$

$$\varepsilon = \varepsilon(\theta, \mathbf{g}, F, \dot{F}),$$

$$\mathbf{q} = \mathbf{q}(\theta, \mathbf{g}, F, \dot{F}),$$

where  $\mathbf{g} = \nabla \theta$ .

By using the chain rule, we can write the material time derivative for  $\eta$ :

$$\dot{\eta} = \frac{\partial \eta}{\partial \theta} \dot{\theta} + \frac{\partial \eta}{\partial \mathbf{g}} \cdot \dot{\mathbf{g}} + \frac{\partial \eta}{\partial F} : \dot{F} + \frac{\partial \eta}{\partial \dot{F}} : \dot{\dot{F}},$$

and, likewise, for  $\varepsilon$ . Here,  $\dot{\dot{F}}$  denotes the material time derivative of  $\dot{F}$ . Substituting the resulting expressions into (2.5), and gathering analogous terms yield

$$\begin{aligned} & \rho \left( \theta \frac{\partial \eta}{\partial \theta} - \frac{\partial \varepsilon}{\partial \theta} \right) \dot{\theta} + \rho \left( \theta \frac{\partial \eta}{\partial \mathbf{g}} - \frac{\partial \varepsilon}{\partial \mathbf{g}} \right) \cdot \dot{\mathbf{g}} + T : D \\ & + \rho \left( \theta \frac{\partial \eta}{\partial F} - \frac{\partial \varepsilon}{\partial F} \right) : \dot{F} + \rho \left( \theta \frac{\partial \eta}{\partial \dot{F}} - \frac{\partial \varepsilon}{\partial \dot{F}} \right) : \dot{\dot{F}} - \frac{\mathbf{q}}{\theta} \cdot \mathbf{g} \geq 0. \end{aligned} \quad (2.6)$$

It can be verified (by appropriate choice of body force and heat radiation term  $r$ ) that at any given place and time, it is possible to find a deformation, stress, and heat flux satisfying the balance laws of momentum and energy and giving to the quantities  $\theta, \mathbf{g}, F, \dot{\theta}, \dot{\mathbf{g}}, \dot{F}, \dot{\dot{F}}$  arbitrarily assigned values. According to the Clausius-Duhem inequality, the left hand side of (2.6) must be non-negative, identically in these six quantities. This implies

$$\begin{aligned} & \theta \frac{\partial \eta}{\partial \theta} - \frac{\partial \varepsilon}{\partial \theta} = 0, \\ & \theta \frac{\partial \eta}{\partial \mathbf{g}} - \frac{\partial \varepsilon}{\partial \mathbf{g}} = 0, \\ & \theta \frac{\partial \eta}{\partial \dot{F}} - \frac{\partial \varepsilon}{\partial \dot{F}} = 0, \\ & \rho \left( \theta \frac{\partial \eta}{\partial F} - \frac{\partial \varepsilon}{\partial F} \right) : \dot{F} + T : D \geq 0, \\ & \frac{\mathbf{q}}{\theta} \cdot \mathbf{g} \leq 0. \end{aligned} \quad (2.7)$$

Using the thermodynamic relation

$$\varepsilon = \psi + \theta \eta,$$

the first equation in (2.7) gives

$$\eta = -\frac{\partial \psi}{\partial \theta},$$

which together with the second and third equations yields

$$\psi = \psi(\theta, F), \quad \eta = \eta(\theta, F), \quad \varepsilon = \varepsilon(\theta, F). \quad (2.8)$$

We now assume that the Cauchy stress tensor can be written as the sum of an elastic and a dissipative contribution

$$T = T^{elas} + T^{visc}.$$

The fourth relation in (2.7) together with the chain rule expression

$$\dot{F} = (\nabla \mathbf{v})F,$$

and equation (2.8) gives

$$T^{elas} = \rho \frac{\partial \psi}{\partial F} F^T.$$

Further, we get the residual inequality

$$T^{visc} : D \geq 0.$$

In the case that Newtonian dissipation is assumed, we get

$$T^{visc} = \nu D,$$

where  $\nu > 0$  denotes the *Newtonian dissipation*. Likewise, a sufficient condition to satisfy the last residual inequality in (2.7) is known as the Fourier law of heat, that is,

$$\mathbf{q} = -\lambda \nabla \theta, \quad \lambda > 0,$$

where  $\lambda$  is the *thermal conductivity*.

## Chapter 3

# Mechanics of Gels

### 3.1 A Mechanical Model of Gels

The system in our consideration consists of a gel and solvent. In the system, the gel is fully submerged under the solvent and assumed to be an incompressible and immiscible mixture of two components, elastic polymer and the same solvent as surroundings. Let the system be fixed and we denote it by  $\mathbb{U}$ . The domain, denoted by  $\Omega$ , where polymer networks occupy in the reference configuration is mapped to a region, represented by  $\Omega_t$ , after time  $t$  by a motion

$$\mathbf{x} = \varphi_t(X) \quad \text{with} \quad \det(\nabla_X \varphi_t(X)) > 0,$$

which is a smooth one to one function that assigns to each point  $X \in \Omega$  a spatial point  $\mathbf{x}$  at time  $t$ . Accordingly, we denote  $\Gamma_t = \partial\Omega_t$  for the boundary of the gel and  $\mathcal{R}_t = \mathbb{U} \setminus (\Omega_t \cup \Gamma_t)$  for the surrounding fluid region. We assume that  $\Gamma_t$  does not touch  $\partial\mathbb{U}$  for all time.

Let  $\mathbf{v}_{1,2,f}$  be the velocities of the polymer and fluid in  $\Omega_t$ , and the fluid in  $\mathcal{R}_t$ , respectively. For simplicity of notation, we use subscripts  $i = 1, 2, f$  in order to refer to polymer, solvent in  $\Omega_t$ , and the outer fluid, respectively. The velocity of polymer  $\mathbf{v}_1$  is defined by

$$\mathbf{v}_1(\mathbf{x}, t) \equiv \frac{\partial \varphi_t(X)}{\partial t}.$$

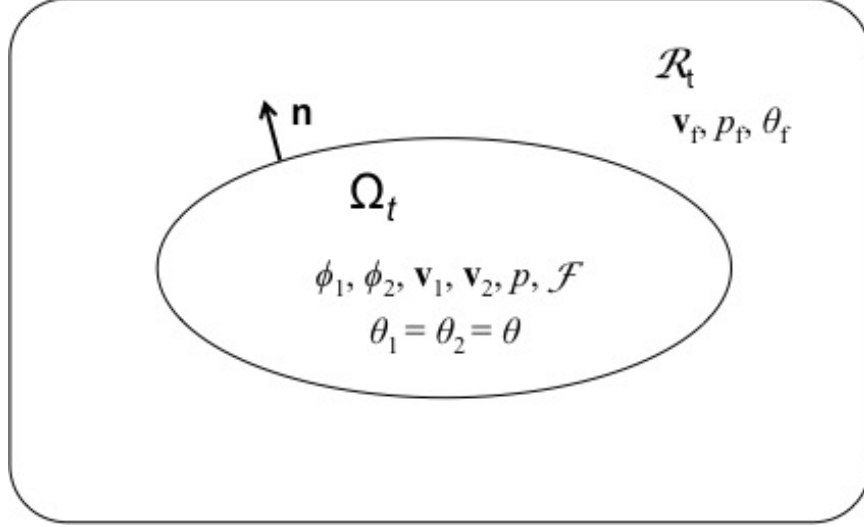


Figure 3.1: **(System Setup)** The system consists of the gel( $\Omega_t$ ) and the surrounding fluid( $\mathcal{R}_t$ ).  $\phi, \mathbf{v}, p, \mathcal{F}, \theta$  represent volume fraction, velocity, pressure, the deformation gradient, and temperature, respectively. Subscripts 1, 2, and  $f$  stand for polymer networks, fluid in and out of the gel in order.

Let  $F = \nabla_X \varphi_t(X)$  be the deformation gradient. Then, for the deformation gradient evaluated in  $\Omega_t$ ,  $\mathcal{F} = F \circ \varphi_t^{-1}$ , it follows that

$$\frac{\partial \mathcal{F}}{\partial t} + (\mathbf{v}_1 \cdot \nabla) \mathcal{F} = (\nabla \mathbf{v}_1) \mathcal{F}. \quad (3.1)$$

We regard that each current position  $\mathbf{x} \in \Omega_t$  holds both polymer and fluid as their portion. The volume fractions of polymer networks and solvent in the gel are denoted by  $\phi_1$  and  $\phi_2$ , respectively, and they satisfy

$$\phi_1 + \phi_2 = 1. \quad (3.2)$$

It is assumed that the two components in the gel have common temperature  $\theta_1(\mathbf{x}, t) = \theta_2(\mathbf{x}, t) = \theta(\mathbf{x}, t) > 0$  at a point  $\mathbf{x}$  in  $\Omega_t$ , and it has the same value on the boundary of the gel as  $\theta_f(\mathbf{x}, t)$ , temperature at  $\mathbf{x}$  in  $\mathcal{R}_t$ . Also, we assume that the temperature on  $\partial\Omega$  keeps constant for all time.

By the incompressibility, the balance of mass for each constituent in the gel can be

written in terms of the volume fraction

$$\frac{\partial \phi_i}{\partial t} + \nabla \cdot (\mathbf{v}_i \phi_i) = 0, \quad (i = 1, 2), \quad (3.3)$$

with which the saturation assumption ( $\phi_1 + \phi_2 = 1$ ) implies

$$\nabla \cdot (\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) = 0. \quad (3.4)$$

The above (3.4) is sometimes called the “*incompressibility condition*” of mixture.

Since we neglect inertial effects, the balance of linear momentum for  $i$ th component in  $\Omega_t$  reduces to

$$\nabla \cdot \mathcal{T}_i - \phi_i \nabla p + \mathbf{f}_i = 0, \quad \mathbf{f}_1 + \mathbf{f}_2 = 0, \quad (3.5)$$

where  $\mathcal{T}_i$  is the Cauchy stress exerting on  $i$ th constituent,  $p$  is the pressure that enforces the incompressibility condition (3.4) and  $\mathbf{f}_i$  is the momentum supply on the component  $i$  due to the local interaction with the other component. We have assumed that there is no external body force. We note that the local mass balance (3.3) can be referentially written as

$$\phi_1 \det \mathcal{F} = \phi_{\text{ref}}, \quad (3.6)$$

where  $\phi_{\text{ref}}$  stands for the volume fraction  $\phi_1$  at time  $t = 0$ .

Similarly, under the assumptions that the fluid is also incompressible and that no body force occurs in  $\mathcal{R}_t$ , we have

$$\nabla \cdot \mathcal{T}_f - \nabla p_f = 0, \quad (3.7)$$

$$\nabla \cdot \mathbf{v}_f = 0. \quad (3.8)$$

We suppose that stresses  $\mathcal{T}_1, \mathcal{T}_2, \mathcal{T}_f$  are given by the following:

$$\begin{aligned} \mathcal{T}_1 &= \mathcal{T}_1^{\text{elas}} + \mathcal{T}_1^{\text{visc}}, \\ \mathcal{T}_{2,f} &= \mathcal{T}_{2,f}^{\text{visc}}, \quad \left( \mathcal{T}_i^{\text{visc}} = \frac{\mu_i}{2} (\nabla \mathbf{v}_i + (\nabla \mathbf{v}_i)^{\text{T}}) = \mu_i \nabla_S \mathbf{v}_i, \quad i = 1, 2, f \right), \end{aligned}$$

where  $\nabla_S \mathbf{v}_i$  indicates the symmetric part of the velocity gradient and  $\mu_{1,2,f}$  represent shear viscosities.

The boundary conditions are given as follows. Let  $\mathbf{n}$  be the unit normal vector which points outward from  $\Omega_t$  to  $\mathcal{R}_t$ . The conservation of mass of fluid gives rise to

$$(\mathbf{v}_f - \mathbf{v}_1) \cdot \mathbf{n} = (1 - \phi_1)(\mathbf{v}_2 - \mathbf{v}_1) \cdot \mathbf{n} \equiv w, \quad (3.9)$$

and moreover no-slip along the surface  $\Gamma_t$  is imposed:

$$(\mathbf{v}_f - \mathbf{v}_1)_{\parallel} = (\mathbf{v}_2 - \mathbf{v}_1)_{\parallel} \equiv \mathbf{r}. \quad (3.10)$$

The force balance across the interface  $\Gamma_t$  is

$$\mathcal{T}_f \mathbf{n} - \mathcal{T}_2 \mathbf{n} - \mathcal{T}_1 \mathbf{n} + [p] \mathbf{n} = 0, \quad ([p] = p - p_f). \quad (3.11)$$

Finally, on  $\partial\mathcal{U}$ , we set

$$\mathbf{v}_f = 0. \quad (3.12)$$

## Chapter 4

# A Theory of Thermal Effects in Gels

In this chapter, we concern two laws of thermodynamics, balance of energy and entropy inequality. In particular, a control volume approach is used. Let  $\omega_0$  be a small fixed volume in time inside  $\Omega_t$ . We first set up the equations of balance of energy and additional boundary conditions, and from these we derive the evolution equations for temperatures  $\theta$  and  $\theta_f$  as well as constitutive restrictions. Then Galilean relativity is discussed.

The independent variables are given by  $\phi_1, \phi_2, \theta, \theta_f, p, p_f, \mathcal{T}_1^{\text{elas}}, \mathbf{v}_i$ , ( $i = 1, 2, f$ ). Densities of the internal energy, the free energy, and the entropy of the gel and surrounding fluid, and heat flux vectors into  $\Omega_t$  and  $\mathcal{R}_t$  across  $\Gamma_t$  are represented by  $\varepsilon, \varepsilon_f, \psi, \psi_f, \eta, \eta_f, \mathbf{q}, \mathbf{q}_f$ , respectively, in which first six are density functions per unit volume and the last two the ones per unit area. We postulate constitutive equations of the form

$$\begin{aligned}\mathcal{T}_1^{\text{elas}} &= \mathcal{T}_1^{\text{elas}}(\mathcal{F}, \phi_1, \phi_2, \theta), \\ \varepsilon &= \varepsilon(\mathcal{F}, \phi_1, \phi_2, \theta), \\ \psi &= \psi(\mathcal{F}, \phi_1, \phi_2, \theta), \\ \eta &= \eta(\mathcal{F}, \phi_1, \phi_2, \theta), \\ \mathbf{q} &= \mathbf{q}(\mathcal{F}, \phi_1, \phi_2, \theta, \nabla\theta),\end{aligned}$$



and

$$\begin{aligned}\varepsilon_f &= \varepsilon_f(\theta_f), \\ \psi_f &= \psi_f(\theta_f), \\ \eta_f &= \eta_f(\theta_f), \\ \mathbf{q}_f &= \mathbf{q}_f(\theta_f, \nabla\theta_f).\end{aligned}$$

We assume that the system  $\mathbb{U}$  is adiabatic. Forms of constitutive equations are constrained by the Second Law of Thermodynamics, which requires that entropy in an isolated system is not decreasing in time.

## 4.1 Energy Balance

Let  $\varepsilon_i$ , ( $i = 1, 2, f$ ), be the internal energy density functions for each component  $i$ . Then the internal energy density  $\varepsilon$  for the whole gel may be written by

$$\varepsilon = \phi_1\varepsilon_1 + \phi_2\varepsilon_2. \quad (4.1)$$

Under the assumption that external heat is not supplied, the first law of thermodynamics in the control volume  $\omega_0$  is stated that the amount of change of internal energy in a fixed volume  $\omega_0$  in time is equal to the sum of energy flux across the boundary of  $\omega_0$ , power expended on the boundary, and the heat flux through the boundary, and it has the form

$$\begin{aligned}\frac{d}{dt} \int_{\omega_0} \varepsilon d\mathbf{x} &= - \int_{\partial\omega_0} (\phi_1\varepsilon_1\mathbf{v}_1 + \phi_2\varepsilon_2\mathbf{v}_2) \cdot \mathbf{n} dA \\ &\quad + \int_{\partial\omega_0} [(\mathcal{T}_1 - \phi_1p\mathbf{I})\mathbf{v}_1 \cdot \mathbf{n} + (\mathcal{T}_2 - \phi_2p\mathbf{I})\mathbf{v}_2 \cdot \mathbf{n}] dA - \int_{\partial\omega_0} \mathbf{q} \cdot \mathbf{n} dA.\end{aligned}$$

Since  $\omega_0$  is arbitrary, this leads to the local form of balance of energy in  $\Omega_t$ :

$$\frac{\partial\varepsilon}{\partial t} + \nabla \cdot (\phi_1\varepsilon_1\mathbf{v}_1 + \phi_2\varepsilon_2\mathbf{v}_2) = \nabla \cdot \left( \mathcal{T}_1\mathbf{v}_1 + \mathcal{T}_2\mathbf{v}_2 - p(\phi_1\mathbf{v}_1 + \phi_2\mathbf{v}_2) - \mathbf{q} \right). \quad (4.2)$$

Similarly, the local version of energy balance in  $\mathcal{R}_t$  is

$$\frac{\partial\varepsilon_f}{\partial t} + \nabla \cdot (\varepsilon_f\mathbf{v}_f) = \nabla \cdot (\mathcal{T}_f\mathbf{v}_f - p_f\mathbf{v}_f - \mathbf{q}_f). \quad (4.3)$$

The energy conservation in the system allows an equation on the interface  $\Gamma_t$ :

$$(\varepsilon_f - \varepsilon_2 - [p])w + \frac{(\mathbf{n} \cdot \mathcal{T}_2 \mathbf{n})}{\phi_2} w - \mathbf{n} \cdot (\mathcal{T}_f \mathbf{n}) w - \mathcal{T}_1 \mathbf{n} \cdot \mathbf{r} + (\mathbf{q}_f - \mathbf{q}) \cdot \mathbf{n} = 0. \quad (4.4)$$

This boundary condition is obtained as follows. Consider a tiny volume  $\bar{\omega}$  which  $\Gamma_t$  cuts through and moves along the interface. Let  $U$  be the total internal energy in the volume  $\bar{\omega}$ . The rate of change of  $U$  is expressed as

$$\frac{dU}{dt} = \frac{d}{dt} \int_{\bar{\omega} \cap \Omega_t} \varepsilon \, d\mathbf{x} + \frac{d}{dt} \int_{\bar{\omega} \cap \mathcal{R}_t} \varepsilon_f \, d\mathbf{x}. \quad (4.5)$$

By applying the Reynolds transport theorem, the first term becomes

$$\begin{aligned} \frac{d}{dt} \int_{\bar{\omega} \cap \Omega_t} \varepsilon \, d\mathbf{x} &= \int_{\bar{\omega} \cap \Omega_t} \frac{\partial \varepsilon}{\partial t} + \nabla \cdot (\mathbf{v}_1 \varepsilon) \, d\mathbf{x} \\ &= \int_{\bar{\omega} \cap \Omega_t} \frac{\partial \varepsilon}{\partial t} \, d\mathbf{x} + \int_{\partial(\bar{\omega} \cap \Omega_t)} \varepsilon \mathbf{v}_1 \cdot \mathbf{n} \, dA. \end{aligned} \quad (4.6)$$

By use of equations (4.1)-(4.2), (4.6) can be written as

$$\begin{aligned} &\int_{\bar{\omega} \cap \Omega_t} -\nabla \cdot (\phi_1 \varepsilon_1 \mathbf{v}_1 + \phi_2 \varepsilon_2 \mathbf{v}_2) + \nabla \cdot (\mathcal{T}_1 \mathbf{v}_1 + \mathcal{T}_2 \mathbf{v}_2 - p(\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) - \mathbf{q}) \, d\mathbf{x} \\ &+ \int_{\partial(\bar{\omega} \cap \Omega_t)} (\phi_1 \varepsilon_1 + \phi_2 \varepsilon_2) \mathbf{v}_1 \cdot \mathbf{n} \, dA, \end{aligned}$$

which yields

$$\int_{\partial(\bar{\omega} \cap \Omega_t)} -\varepsilon_2 \phi_2 (\mathbf{v}_2 - \mathbf{v}_1) \cdot \mathbf{n} + \mathcal{T}_1 \mathbf{n} \cdot \mathbf{v}_1 + \mathcal{T}_2 \mathbf{n} \cdot \mathbf{v}_2 - p \phi_1 \mathbf{v}_1 \cdot \mathbf{n} - p \phi_2 \mathbf{v}_2 \cdot \mathbf{n} - \mathbf{q} \cdot \mathbf{n} \, dA.$$

Likewise, the second term of (4.5) is computed as

$$\begin{aligned} \frac{d}{dt} \int_{\bar{\omega} \cap \mathcal{R}_t} \varepsilon_f \, d\mathbf{x} &= \int_{\bar{\omega} \cap \mathcal{R}_t} \frac{\partial \varepsilon_f}{\partial t} + \nabla \cdot (\mathbf{v}_1 \varepsilon_f) \, d\mathbf{x} \\ &= \int_{\bar{\omega} \cap \mathcal{R}_t} \frac{\partial \varepsilon_f}{\partial t} \, d\mathbf{x} - \int_{\partial(\bar{\omega} \cap \mathcal{R}_t)} \varepsilon_f \mathbf{v}_1 \cdot \mathbf{n} \, dA \\ &= \int_{\partial(\bar{\omega} \cap \mathcal{R}_t)} \varepsilon_f (\mathbf{v}_f - \mathbf{v}_1) \cdot \mathbf{n} - \mathcal{T}_f \mathbf{n} \cdot \mathbf{v}_f + p_f \mathbf{v}_f \cdot \mathbf{n} + \mathbf{q}_f \cdot \mathbf{n} \, dA. \end{aligned}$$

Since  $\partial(\bar{\omega} \cap \Omega_t) = (\partial \bar{\omega} \cap \Omega_t) \cup (\bar{\omega} \cap \Gamma_t)$  and  $\partial(\bar{\omega} \cap \mathcal{R}_t) = (\partial \bar{\omega} \cap \mathcal{R}_t) \cup (\bar{\omega} \cap \Gamma_t)$ , the first

law of thermodynamics implies

$$\begin{aligned}
0 &= \int_{\bar{\omega} \cap \Gamma_t} -\varepsilon_2 \phi_2 (\mathbf{v}_2 - \mathbf{v}_1) \cdot \mathbf{n} + \mathcal{T}_1 \mathbf{n} \cdot \mathbf{v}_1 + \mathcal{T}_2 \mathbf{n} \cdot \mathbf{v}_2 - p \phi_1 \mathbf{v}_1 \cdot \mathbf{n} - p \phi_2 \mathbf{v}_2 \cdot \mathbf{n} - \mathbf{q} \cdot \mathbf{n} \\
&\quad + \varepsilon_f (\mathbf{v}_f - \mathbf{v}_1) \cdot \mathbf{n} - \mathcal{T}_f \mathbf{n} \cdot \mathbf{v}_f + p_f \mathbf{v}_f \cdot \mathbf{n} + \mathbf{q}_f \cdot \mathbf{n} dA \\
&= \int_{\bar{\omega} \cap \Gamma_t} (\varepsilon_f - \varepsilon_2 - p) w + \mathcal{T}_1 \mathbf{n} \cdot \mathbf{v}_1 + \mathcal{T}_2 \mathbf{n} \cdot \mathbf{v}_2 - \mathcal{T}_f \mathbf{n} \cdot \mathbf{v}_f \\
&\quad + (p_f \mathbf{v}_f - p \mathbf{v}_1) \cdot \mathbf{n} + (\mathbf{q}_f - \mathbf{q}) \cdot \mathbf{n} dA,
\end{aligned}$$

where (3.9) is used, and by the arbitrariness of  $\bar{\omega}$ , we obtain

$$(\varepsilon_f - \varepsilon_2 - p)w + \mathcal{T}_1 \mathbf{n} \cdot \mathbf{v}_1 + \mathcal{T}_2 \mathbf{n} \cdot \mathbf{v}_2 - \mathcal{T}_f \mathbf{n} \cdot \mathbf{v}_f + (p_f \mathbf{v}_f - p \mathbf{v}_1 + \mathbf{q}_f - \mathbf{q}) \cdot \mathbf{n} = 0.$$

Let us simplify this equation. By use of (3.11), we see

$$\begin{aligned}
&\mathcal{T}_1 \mathbf{n} \cdot \mathbf{v}_1 + \mathcal{T}_2 \mathbf{n} \cdot \mathbf{v}_2 - \mathcal{T}_f \mathbf{n} \cdot \mathbf{v}_f \\
&= -\mathcal{T}_f \mathbf{n} \cdot (\mathbf{v}_f - \mathbf{v}_1) + \mathcal{T}_2 \mathbf{n} \cdot (\mathbf{v}_2 - \mathbf{v}_1) + [p] \mathbf{n} \cdot \mathbf{v}_1 \\
&= -\mathcal{T}_f \mathbf{n} \cdot (\mathbf{n}w + \mathbf{r}) + \mathcal{T}_2 \mathbf{n} \cdot \left( \mathbf{n} \frac{w}{\phi_2} + \mathbf{r} \right) + [p] \mathbf{n} \cdot \mathbf{v}_1 \\
&= -\mathbf{n} \cdot (\mathcal{T}_f \mathbf{n}) w - \mathcal{T}_f \mathbf{n} \cdot \mathbf{r} + \frac{(\mathbf{n} \cdot \mathcal{T}_2 \mathbf{n})}{\phi_2} w + \mathcal{T}_2 \mathbf{n} \cdot \mathbf{r} + [p] \mathbf{n} \cdot \mathbf{v}_1,
\end{aligned}$$

and also

$$[p_f \mathbf{v}_f - p \mathbf{v}_1] \cdot \mathbf{n} = [p_f (\mathbf{v}_f - \mathbf{v}_1) + p_f \mathbf{v}_1 - p \mathbf{v}_1] \cdot \mathbf{n} = p_f w - [p] \mathbf{v}_1 \cdot \mathbf{n},$$

therefore we have

$$(\varepsilon_f - \varepsilon_2 - p)w + \frac{(\mathbf{n} \cdot \mathcal{T}_2 \mathbf{n})}{\phi_2} w - \mathbf{n} \cdot (\mathcal{T}_f \mathbf{n}) w - \mathcal{T}_f \mathbf{n} \cdot \mathbf{r} + \mathcal{T}_2 \mathbf{n} \cdot \mathbf{r} + p_f w + (\mathbf{q}_f - \mathbf{q}) \cdot \mathbf{n} = 0.$$

Using (3.11) again results in (4.4):

$$(\varepsilon_f - \varepsilon_2 - [p])w + \frac{(\mathbf{n} \cdot \mathcal{T}_2 \mathbf{n})}{\phi_2} w - \mathbf{n} \cdot (\mathcal{T}_f \mathbf{n}) w - \mathcal{T}_1 \mathbf{n} \cdot \mathbf{r} + (\mathbf{q}_f - \mathbf{q}) \cdot \mathbf{n} = 0.$$

## 4.2 Boundary Conditions Deduced by Thermodynamics Second Law

Some boundary conditions are deduced by considering variations in temperature. We take the entropy into consideration. Let us denote the entropy density functions by

$\eta_i$ , ( $i = 1, 2, f$ ), for each constituent  $i$  and by  $\eta = \phi_1\eta_1 + \phi_2\eta_2$  for the entire gel,  $\Omega_t$ . For any fixed  $\omega_0$ , as in the preceding section, the change of entropy in time can be written as

$$\frac{d}{dt} \int_{\omega_0} \eta \, d\mathbf{x} = - \int_{\partial\omega_0} (\phi_1\eta_1\mathbf{v}_1 + \phi_2\eta_2\mathbf{v}_2) \cdot \mathbf{n} \, dA - \int_{\partial\omega_0} \frac{\mathbf{q}}{\theta} \cdot \mathbf{n} \, dA + \int_{\omega_0} Q \, d\mathbf{x},$$

where the first and second integrals on the right hand side represent the rates of entropy flow across  $\partial\omega_0$  conveyed by the material coming in due to convection and caused by heat, respectively, and the third integral represents the net entropy production. Since  $\omega_0$  was arbitrary, we have the local version of the second law of thermodynamics:

$$\frac{\partial\eta}{\partial t} + \nabla \cdot (\phi_1\eta_1\mathbf{v}_1 + \phi_2\eta_2\mathbf{v}_2) + \nabla \cdot \left( \frac{\mathbf{q}}{\theta} \right) = Q \geq 0, \quad \text{in } \Omega_t. \quad (4.7)$$

In the same way, the local form in  $\mathcal{R}_t$  is given by

$$\frac{\partial\eta_f}{\partial t} + \nabla \cdot (\eta_f\mathbf{v}_f) + \nabla \cdot \left( \frac{\mathbf{q}_f}{\theta_f} \right) = Q_f \geq 0. \quad (4.8)$$

Here,  $Q$  and  $Q_f$  mean the respective net entropy production densities in  $\Omega_t$  and  $\mathcal{R}_t$ .

Now we claim that

$$\frac{d}{dt} \int_{\mathbb{U}} \eta \, d\mathbf{x} = \int_{\Omega_t} Q \, d\mathbf{x} + \int_{\mathcal{R}_t} Q_f \, d\mathbf{x} + \int_{\Gamma_t} Q_\Gamma \, dA, \quad (4.9)$$

where

$$Q_\Gamma = (\eta_f - \eta_2) w + \left( \frac{\mathbf{q}_f}{\theta_f} - \frac{\mathbf{q}}{\theta} \right) \cdot \mathbf{n}, \quad (4.10)$$

and the second law of thermodynamics implies that

$$Q_\Gamma \geq 0. \quad (4.11)$$

The following is the proof of (4.9). First we use the Reynolds transport theorem,

(4.7) and (3.9) to get

$$\begin{aligned}
& \frac{d}{dt} \int_{\Omega_t} \eta \, d\mathbf{x} \\
&= \int_{\Omega_t} \frac{\partial \eta}{\partial t} \, d\mathbf{x} + \int_{\Gamma_t} \eta \mathbf{v}_1 \cdot \mathbf{n} \, dA \\
&= \int_{\Omega_t} -\nabla \cdot (\phi_1 \eta_1 \mathbf{v}_1 + \phi_2 \eta_2 \mathbf{v}_2) - \nabla \cdot \left( \frac{\mathbf{q}}{\theta} \right) + Q \, d\mathbf{x} + \int_{\Gamma_t} (\phi_1 \eta_1 + \phi_2 \eta_2) \mathbf{v}_1 \cdot \mathbf{n} \, dA \\
&= \int_{\Omega_t} Q \, d\mathbf{x} + \int_{\Gamma_t} -(\phi_1 \eta_1 \mathbf{v}_1 + \phi_2 \eta_2 \mathbf{v}_2) \cdot \mathbf{n} - \frac{\mathbf{q}}{\theta} \cdot \mathbf{n} + (\phi_1 \eta_1 + \phi_2 \eta_2) \mathbf{v}_1 \cdot \mathbf{n} \, dA \\
&= \int_{\Omega_t} Q \, d\mathbf{x} + \int_{\Gamma_t} -\eta_2 \phi_2 (\mathbf{v}_2 - \mathbf{v}_1) \cdot \mathbf{n} - \frac{\mathbf{q}}{\theta} \cdot \mathbf{n} \, dA \\
&= \int_{\Omega_t} Q \, d\mathbf{x} + \int_{\Gamma_t} -\eta_2 w - \frac{\mathbf{q}}{\theta} \cdot \mathbf{n} \, dA.
\end{aligned}$$

A similar computation provides

$$\frac{d}{dt} \int_{\mathcal{R}_t} \eta_f \, d\mathbf{x} = \int_{\mathcal{R}_t} Q_f \, d\mathbf{x} + \int_{\Gamma_t} \eta_f w + \frac{\mathbf{q}_f}{\theta_f} \cdot \mathbf{n} \, dA,$$

and sum of these two results brings the equation (4.9), since

$$\frac{d}{dt} \int_{\mathbb{U}} \eta \, d\mathbf{x} = \frac{d}{dt} \int_{\Omega_t} \eta \, d\mathbf{x} + \frac{d}{dt} \int_{\mathcal{R}_t} \eta_f \, d\mathbf{x}.$$

Using (4.4) and thermodynamic relations  $\varepsilon_i = \psi_i + \theta_i \eta_i$ , ( $i = 1, 2, f$ ), in conjunction with the assumption that  $\theta = \theta_f$  on  $\Gamma_t$ , (4.10) takes the form

$$\begin{aligned}
Q_\Gamma &= (\eta_f - \eta_2) w + \left( \frac{\mathbf{q}_f}{\theta_f} - \frac{\mathbf{q}}{\theta} \right) \cdot \mathbf{n} \\
&= (\eta_f - \eta_2) w + \frac{1}{\theta} (\mathbf{q}_f - \mathbf{q}) \cdot \mathbf{n} \\
&= \frac{1}{\theta} \left( \mathbf{n} \cdot (\mathcal{T}_f \mathbf{n}) - \mathbf{n} \cdot \left( \frac{\mathcal{T}_2}{\phi_2} \right) \mathbf{n} + [p] + (\psi_2 - \psi_f) \right) w + \frac{1}{\theta} (\mathcal{T}_1 \mathbf{n} \cdot \mathbf{r}).
\end{aligned}$$

From (4.11) we can impose the boundary conditions on  $\Gamma_t$ :

$$\mu_\perp w = \mathbf{n} \cdot (\mathcal{T}_f \mathbf{n}) - \mathbf{n} \cdot \left( \frac{\mathcal{T}_2}{\phi_2} \right) \mathbf{n} + [p] + (\psi_2 - \psi_f), \quad (4.12)$$

$$\mu_\parallel \mathbf{r} = (\mathcal{T}_1 \mathbf{n})_\parallel, \quad (4.13)$$

where  $\mu_\perp$  and  $\mu_\parallel$  are non-negative constants.

### 4.3 Evolution Equations for Temperature

In this section we derive equations for temperature development in time of the system. In order to obtain them, first of all, we must specify  $\mathcal{T}_i, \mathbf{f}_i, \varepsilon, \varepsilon_i$  and  $\mathbf{q}, \mathbf{q}_f$ . We shall take as our starting point an expression for the Helmholtz free energy density  $\psi$  in terms of  $\phi_1, \mathcal{F}$  and  $\theta$ . We recall that  $\mathcal{F}$  satisfies the equations

$$\frac{\partial}{\partial t} \mathcal{F} + \mathbf{v}_1 \cdot \nabla \mathcal{F} = (\nabla \mathbf{v}_1) \mathcal{F}, \quad (4.14)$$

$$\phi_1 \det \mathcal{F} = \phi_{\text{ref}}. \quad (4.15)$$

Given  $\psi(\phi_1, \mathcal{F}, \theta)$ , from the usual thermodynamic relations, we have

$$\varepsilon = \psi + \theta \eta, \quad \eta = -\frac{\partial \psi}{\partial \theta}. \quad (4.16)$$

We need expressions for  $\varepsilon_i$ . The crucial insight here is that it is possible to determine the expressions for  $\varepsilon_i$  given only the expression for  $\varepsilon$ . Note that (4.1) is hardly sufficient to obtain an expression for  $\varepsilon_i$  given  $\varepsilon$ .

Consider a spatially uniform gel of volume  $V$ , so that  $\phi_1, \mathcal{F}$  and  $\theta$  take the same values everywhere. The total energy  $E$  of this gel is given by

$$E = V \varepsilon(\phi_1, \mathcal{F}, \theta). \quad (4.17)$$

Define

$$V_i = V \phi_i, \quad \mathcal{G} = (\det \mathcal{F})^{-1/3} \mathcal{F} = \left( \frac{\phi_1}{\phi_{\text{ref}}} \right)^{1/3} \mathcal{F}. \quad (4.18)$$

View  $E$  as a function of  $V_i, \mathcal{G}$  and  $\theta$  instead of  $V, \phi_i, \mathcal{F}$  and  $\theta$ , and call this function  $\widehat{E}$

$$\widehat{E}(V_1, V_2, \mathcal{G}, \theta) = (V_1 + V_2) \varepsilon \left( \frac{V_1}{V_1 + V_2}, \phi_{\text{ref}}^{1/3} \left( \frac{V_1}{V_1 + V_2} \right)^{-1/3} \mathcal{G}, \theta \right). \quad (4.19)$$

The energy per unit volume of polymer and fluid should be given as the partial derivative of  $\widehat{E}$  with respect to  $V_1$  and  $V_2$  respectively

$$\widehat{\varepsilon}_i = \frac{\partial \widehat{E}}{\partial V_i}. \quad (4.20)$$

We have used the symbol  $\widehat{\varepsilon}_i$  to emphasize the fact that  $\widehat{\varepsilon}_i$  is a function of  $V_1, V_2, \mathcal{G}$  and  $\theta$  instead of  $\phi_1, \mathcal{F}$  and  $\theta$ . The function  $\widehat{E}$  is a one-homogeneous function in  $V_1$  and  $V_2$

$$\widehat{E}(sV_1, sV_2, \mathcal{G}, \theta) = s\widehat{E}(V_1, V_2, \mathcal{G}, \theta) \quad \text{for } s > 0. \quad (4.21)$$

By taking the derivative of the above in  $s$  and letting  $s = 1$ , we have (Euler's formula for homogeneous functions)

$$\widehat{E} = V_1 \frac{\partial \widehat{E}}{\partial V_1} + V_2 \frac{\partial \widehat{E}}{\partial V_2} = V_1 \widehat{\varepsilon}_1 + V_2 \widehat{\varepsilon}_2. \quad (4.22)$$

Dividing by  $V$ , we have

$$\widehat{\varepsilon} = \frac{\widehat{E}}{V} = \frac{V_1}{V} \widehat{\varepsilon}_1 + \frac{V_2}{V} \widehat{\varepsilon}_2 = \phi_1 \widehat{\varepsilon}_1 + \phi_2 \widehat{\varepsilon}_2. \quad (4.23)$$

This is nothing other than (4.1) except that the functions are in terms of  $V_1, V_2, \mathcal{G}$  and  $\theta$ . For the above expressions to be useful, we must check that they are independent of the arbitrary volume parameter  $V$ . This can be seen as follows. Dividing (4.19) by  $V$ , we see that  $\widehat{\varepsilon}$  may be viewed as a function of  $\phi_1$  and  $\phi_2$  instead of  $V_1$  and  $V_2$

$$\widehat{\varepsilon}(\phi_1, \phi_2, \mathcal{G}, \theta) = (\phi_1 + \phi_2) \varepsilon \left( \frac{\phi_1}{\phi_1 + \phi_2}, \phi_{\text{ref}}^{1/3} \left( \frac{\phi_1}{\phi_1 + \phi_2} \right)^{-1/3} \mathcal{G}, \theta \right). \quad (4.24)$$

It is easily checked that (4.20) is equivalent to the following

$$\widehat{\varepsilon}_i(\phi_1, \phi_2, \mathcal{G}, \theta) = \frac{\partial \widehat{\varepsilon}}{\partial \phi_i}. \quad (4.25)$$

We shall henceforth view  $\widehat{\varepsilon}, \widehat{\varepsilon}_i$  as functions of  $\phi_1, \phi_2, \mathcal{G}$  and  $\theta$  instead of  $V_1, V_2, \mathcal{G}$  and  $\theta$ . By restricting  $\widehat{\varepsilon}_i$  to  $\phi_1 + \phi_2 = 1$ , we obtain the expressions for  $\varepsilon_i$  in terms of  $\phi_1, \mathcal{F}$  and  $\theta$

$$\varepsilon_i(\phi_1, \mathcal{F}, \theta) = \widehat{\varepsilon}_i \left( \phi_1, 1 - \phi_1, \left( \frac{\phi_1}{\phi_{\text{ref}}} \right)^{1/3} \mathcal{F}, \theta \right). \quad (4.26)$$

Similarly to  $\widehat{\varepsilon}$ , we define  $\widehat{\psi}, \widehat{\psi}_i, \widehat{\eta}$  and  $\widehat{\eta}_i$  as follows.

$$\widehat{\psi}(\phi_1, \phi_2, \mathcal{G}, \theta) = (\phi_1 + \phi_2) \psi \left( \frac{\phi_1}{\phi_1 + \phi_2}, \phi_{\text{ref}}^{1/3} \left( \frac{\phi_1}{\phi_1 + \phi_2} \right)^{-1/3} \mathcal{G}, \theta \right), \quad (4.27)$$

$$\widehat{\eta}(\phi_1, \phi_2, \mathcal{G}, \theta) = (\phi_1 + \phi_2) \eta \left( \frac{\phi_1}{\phi_1 + \phi_2}, \phi_{\text{ref}}^{1/3} \left( \frac{\phi_1}{\phi_1 + \phi_2} \right)^{-1/3} \mathcal{G}, \theta \right), \quad (4.28)$$

$$\widehat{\psi}_i = \frac{\partial \widehat{\psi}}{\partial \phi_i}, \quad \widehat{\eta}_i = \frac{\partial \widehat{\eta}}{\partial \phi_i}. \quad (4.29)$$

Note that, similarly to  $\psi, \varepsilon$  and  $\eta$ , the above quantities are also related to one another through (4.16).

Given expressions for  $\varepsilon_i$  in terms of  $\varepsilon$ , we now simplify (4.2). The left hand side of (4.2) yields

$$\begin{aligned} & \frac{\partial \varepsilon}{\partial t} + \nabla \cdot (\phi_1 \varepsilon_1 \mathbf{v}_1 + \phi_2 \varepsilon_2 \mathbf{v}_2) \\ &= \frac{\partial \widehat{\varepsilon}}{\partial \phi_1} \frac{\partial \phi_1}{\partial t} + \frac{\partial \widehat{\varepsilon}}{\partial \phi_2} \frac{\partial \phi_2}{\partial t} + \frac{\partial \widehat{\varepsilon}}{\partial \mathcal{G}} : \frac{\partial \mathcal{G}}{\partial t} + \frac{\partial \widehat{\varepsilon}}{\partial \theta} \frac{\partial \theta}{\partial t} + \nabla \cdot (\phi_1 \varepsilon_1 \mathbf{v}_1 + \phi_2 \varepsilon_2 \mathbf{v}_2). \end{aligned} \quad (4.30)$$

We have

$$\begin{aligned} & \frac{\partial \widehat{\varepsilon}}{\partial \phi_1} \frac{\partial \phi_1}{\partial t} + \frac{\partial \widehat{\varepsilon}}{\partial \phi_2} \frac{\partial \phi_2}{\partial t} + \nabla \cdot (\phi_1 \varepsilon_1 \mathbf{v}_1 + \phi_2 \varepsilon_2 \mathbf{v}_2) \\ &= -\frac{\partial \widehat{\varepsilon}}{\partial \phi_1} \nabla \cdot (\phi_1 \mathbf{v}_1) - \frac{\partial \widehat{\varepsilon}}{\partial \phi_2} \nabla \cdot (\phi_2 \mathbf{v}_2) + \nabla \cdot \left( \phi_1 \frac{\partial \widehat{\varepsilon}}{\partial \phi_1} \mathbf{v}_1 + \phi_2 \frac{\partial \widehat{\varepsilon}}{\partial \phi_2} \mathbf{v}_2 \right) \\ &= \phi_1 \mathbf{v}_1 \cdot \nabla \left( \frac{\partial \widehat{\varepsilon}}{\partial \phi_1} \right) + \phi_2 \mathbf{v}_2 \cdot \nabla \left( \frac{\partial \widehat{\varepsilon}}{\partial \phi_2} \right), \end{aligned} \quad (4.31)$$

where we used (3.3) and (4.25) in the first equality. The third term in the last line of (4.30) can be written as

$$\begin{aligned} \frac{\partial \widehat{\varepsilon}}{\partial \mathcal{G}} : \frac{\partial \mathcal{G}}{\partial t} &= \phi_{\text{ref}}^{1/3} (\phi_1 + \phi_2)^{4/3} \phi_1^{-1/3} \frac{\partial \varepsilon}{\partial \mathcal{F}} : \frac{\partial}{\partial t} (\phi_{\text{ref}}^{-1/3} \phi_1^{1/3} \mathcal{F}) \\ &= \frac{1}{3} \phi_1^{-1} \frac{\partial \phi_1}{\partial t} \frac{\partial \varepsilon}{\partial \mathcal{F}} : \mathcal{F} + \frac{\partial \varepsilon}{\partial \mathcal{F}} : \frac{\partial \mathcal{F}}{\partial t} \\ &= -\frac{1}{3} \phi_1^{-1} \nabla \cdot (\phi_1 \mathbf{v}_1) \frac{\partial \varepsilon}{\partial \mathcal{F}} : \mathcal{F} + \frac{\partial \varepsilon}{\partial \mathcal{F}} : (-\mathbf{v}_1 \cdot \nabla \mathcal{F} + \nabla \mathbf{v}_1 \mathcal{F}) \\ &= -\mathbf{v}_1 \cdot \left( \frac{1}{3} \phi_1^{-1} \nabla \phi_1 \left( \frac{\partial \varepsilon}{\partial \mathcal{F}} : \mathcal{F} \right) + \frac{\partial \varepsilon}{\partial \mathcal{F}} : \nabla \mathcal{F} \right) \\ &\quad + \nabla \mathbf{v}_1 : \left( \frac{\partial \varepsilon}{\partial \mathcal{F}} \mathcal{F}^T - \frac{1}{3} \left( \frac{\partial \varepsilon}{\partial \mathcal{F}} : \mathcal{F} \right) I \right), \\ \left( \frac{\partial \varepsilon}{\partial \mathcal{F}} : \nabla \mathcal{F} \right)_k &= \sum_{i,j} \frac{\partial \varepsilon}{\partial \mathcal{F}_{ij}} \frac{\partial}{\partial x_k} \mathcal{F}_{ij}, \end{aligned} \quad (4.32)$$

where  $I$  is the  $3 \times 3$  identity matrix,  $(\cdot)_k$  denotes the  $k$ -th component of a vector,  $x_k$  are the Cartesian spatial coordinates and  $\mathcal{F}_{ij}$  denotes the  $ij$  element of the deformation gradient. We used (4.24), (4.18) in the first equality, (3.2) in the second equality and (3.3) and (4.14) in the third equality.



The right hand side of (4.2) yields

$$\begin{aligned} & \nabla \cdot (\mathcal{T}_1 \mathbf{v}_1 + \mathcal{T}_2 \mathbf{v}_2 - p(\phi_1 \mathbf{v}_1 + \phi_2 \mathbf{v}_2) - \mathbf{q}) \\ &= \mathcal{T}_1 : (\nabla \mathbf{v}_1) + \mathcal{T}_2 : (\nabla \mathbf{v}_2) - \mathbf{f}_1 \cdot \mathbf{v}_1 - \mathbf{f}_2 \cdot \mathbf{v}_2 - \nabla \cdot \mathbf{q}, \end{aligned} \quad (4.33)$$

where we used (3.5). Combining (4.30), (4.31), (4.32) and (4.33), we find that (4.2) can be rewritten as follows.

$$\begin{aligned} C_v \frac{\partial \theta}{\partial t} &= \mathbf{v}_1 \cdot \left( -\phi_1 \nabla \left( \frac{\partial \widehat{\varepsilon}}{\partial \phi_1} \right) + \frac{1}{3} \phi_1^{-1} \nabla \phi_1 \left( \frac{\partial \varepsilon}{\partial \mathcal{F}} : \mathcal{F} \right) + \frac{\partial \varepsilon}{\partial \mathcal{F}} : \nabla \mathcal{F} - \mathbf{f}_1 \right) \\ &+ \nabla \mathbf{v}_1 : \left( \mathcal{T}_1 - \frac{\partial \varepsilon}{\partial \mathcal{F}} \mathcal{F}^T + \frac{1}{3} \left( \frac{\partial \varepsilon}{\partial \mathcal{F}} : \mathcal{F} \right) I \right) \\ &- \mathbf{v}_2 \cdot \left( \phi_2 \nabla \left( \frac{\partial \widehat{\varepsilon}}{\partial \phi_2} \right) + \mathbf{f}_2 \right) + \mathcal{T}_2 : (\nabla \mathbf{v}_2) - \nabla \cdot \mathbf{q}, \end{aligned} \quad (4.34)$$

where  $C_v = \partial \widehat{\varepsilon} / \partial \theta$  is the heat capacity at constant volume in  $\Omega_t$ .

Because  $\varepsilon_f$  depends only on temperature, (4.3) can be expressed as

$$\frac{\partial \varepsilon_f}{\partial \theta_f} \frac{\partial \theta_f}{\partial t} + \mathbf{v}_f \cdot \nabla \varepsilon_f = \mathcal{T}_f : \nabla \mathbf{v}_f + \mathbf{v}_f \cdot (\nabla \cdot \mathcal{T}_f) - \mathbf{v}_f \cdot \nabla p_f - \nabla \cdot \mathbf{q}_f, \quad (4.35)$$

where (3.8) has been used. By (3.7), (4.35) is reduced to

$$C_{fv} \frac{\partial \theta_f}{\partial t} = \mathcal{T}_f : \nabla \mathbf{v}_f - \mathbf{v}_f \cdot \nabla \varepsilon_f - \nabla \cdot \mathbf{q}_f, \quad (4.36)$$

as above  $C_{fv} = \partial \varepsilon_f / \partial \theta_f$  denotes the heat capacity at constant volume in  $\mathcal{R}_t$ .

## 4.4 Entropy Inequality and the Resulting Relations

The purpose of this section is to derive thermodynamic restrictions of the system from the entropy inequality. The same point of view is taken for the energy and entropy densities as in Section 4.3.

We have seen in Section 4.2 that the local form of the net entropy production inside the gel was given by (4.7):

$$Q = \frac{\partial \eta}{\partial t} + \nabla \cdot (\phi_1 \eta_1 \mathbf{v}_1 + \phi_2 \eta_2 \mathbf{v}_2) + \nabla \cdot \left( \frac{\mathbf{q}}{\theta} \right),$$

which can be written by the chain rule as

$$Q = \frac{\partial \hat{\eta}}{\partial \phi_1} \frac{\partial \phi_1}{\partial t} + \frac{\partial \hat{\eta}}{\partial \phi_2} \frac{\partial \phi_2}{\partial t} + \frac{\partial \hat{\eta}}{\partial \mathcal{G}} : \frac{\partial \mathcal{G}}{\partial t} + \frac{\partial \hat{\eta}}{\partial \theta} \frac{\partial \theta}{\partial t} + \nabla \cdot (\phi_1 \eta_1 \mathbf{v}_1 + \phi_2 \eta_2 \mathbf{v}_2) + \nabla \cdot \left( \frac{\mathbf{q}}{\theta} \right). \quad (4.37)$$

Some calculus similar to (4.31)-(4.32) and

$$\frac{\partial \hat{\eta}}{\partial \theta} \frac{\partial \theta}{\partial t} = \frac{1}{\theta} \frac{\partial \hat{\varepsilon}}{\partial \theta} \frac{\partial \theta}{\partial t} = \frac{1}{\theta} C_v \frac{\partial \theta}{\partial t} \quad (4.38)$$

lead (4.37) to

$$\begin{aligned} Q &= \phi_1 \mathbf{v}_1 \cdot \nabla \left( \frac{\partial \hat{\eta}}{\partial \phi_1} \right) + \phi_2 \mathbf{v}_2 \cdot \nabla \left( \frac{\partial \hat{\eta}}{\partial \phi_2} \right) - \mathbf{v}_1 \cdot \left( \frac{1}{3} \phi_1^{-1} \nabla \phi_1 \left( \frac{\partial \eta}{\partial \mathcal{F}} : \mathcal{F} \right) + \frac{\partial \eta}{\partial \mathcal{F}} : \nabla \mathcal{F} \right) \\ &\quad + \nabla \mathbf{v}_1 : \left( \frac{\partial \eta}{\partial \mathcal{F}} \mathcal{F}^T - \frac{1}{3} \left( \frac{\partial \eta}{\partial \mathcal{F}} : \mathcal{F} \right) \mathbf{I} \right) + \frac{1}{\theta} C_v \frac{\partial \theta}{\partial t} + \nabla \cdot \left( \frac{\mathbf{q}}{\theta} \right). \end{aligned}$$

Using (4.34), then by collecting like terms, we have

$$Q = \frac{1}{\theta} \left( \mathbf{v}_1 \cdot (\mathbf{g}_1 - \mathbf{f}_1) + \mathbf{v}_2 \cdot (\mathbf{g}_2 - \mathbf{f}_2) + (\nabla \mathbf{v}_1) : (\mathcal{T}_1 - \mathcal{T}_1^{\text{elas}}) + (\nabla \mathbf{v}_2) : \mathcal{T}_2 \right) - \frac{1}{\theta^2} (\mathbf{q} \cdot \nabla \theta),$$

where

$$\begin{aligned} \mathbf{g}_1 &= -\phi_1 \left( \nabla \left( \frac{\partial \hat{\varepsilon}}{\partial \phi_1} \right) - \theta \nabla \left( \frac{\partial \hat{\eta}}{\partial \phi_1} \right) \right) + \frac{1}{3\phi_1} \nabla \phi_1 \left( \frac{\partial \psi}{\partial \mathcal{F}} : \mathcal{F} \right) + \frac{\partial \psi}{\partial \mathcal{F}} : \nabla \mathcal{F}, \\ \mathbf{g}_2 &= -\phi_2 \left( \nabla \left( \frac{\partial \hat{\varepsilon}}{\partial \phi_2} \right) - \theta \nabla \left( \frac{\partial \hat{\eta}}{\partial \phi_2} \right) \right), \\ \mathcal{T}_1^{\text{elas}} &= \frac{\partial \psi}{\partial \mathcal{F}} \mathcal{F}^T - \frac{1}{3} \left( \frac{\partial \psi}{\partial \mathcal{F}} : \mathcal{F} \right) \mathbf{I}. \end{aligned} \quad (4.39)$$

We now claim that

$$\mathbf{g}_1 + \mathbf{g}_2 = 0. \quad (4.40)$$

By (4.23) and (4.26), we have

$$\hat{\varepsilon} = \phi_1 \frac{\partial \hat{\varepsilon}}{\partial \phi_1} + \phi_2 \frac{\partial \hat{\varepsilon}}{\partial \phi_2}. \quad (4.41)$$

Take the gradient on both sides of the above

$$\frac{\partial \hat{\varepsilon}}{\partial \mathcal{G}} : \nabla \mathcal{G} + \frac{\partial \hat{\varepsilon}}{\partial \theta} \nabla \theta = \phi_1 \nabla \left( \frac{\partial \hat{\varepsilon}}{\partial \phi_1} \right) + \phi_2 \nabla \left( \frac{\partial \hat{\varepsilon}}{\partial \phi_2} \right). \quad (4.42)$$

Proceeding as in the first line of (4.32), we have

$$\frac{1}{3}\phi_1^{-1}\nabla\phi_1\left(\frac{\partial\varepsilon}{\partial\mathcal{F}}:\mathcal{F}\right)+\frac{\partial\varepsilon}{\partial\mathcal{F}}:\nabla\mathcal{F}+\frac{\partial\widehat{\varepsilon}}{\partial\theta}\nabla\theta=\phi_1\nabla\left(\frac{\partial\widehat{\varepsilon}}{\partial\phi_1}\right)+\phi_2\nabla\left(\frac{\partial\widehat{\varepsilon}}{\partial\phi_2}\right). \quad (4.43)$$

In exactly the same fashion, we find that

$$\frac{1}{3}\phi_1^{-1}\nabla\phi_1\left(\frac{\partial\eta}{\partial\mathcal{F}}:\mathcal{F}\right)+\frac{\partial\eta}{\partial\mathcal{F}}:\nabla\mathcal{F}+\frac{\partial\widehat{\eta}}{\partial\theta}\nabla\theta=\phi_1\nabla\left(\frac{\partial\widehat{\eta}}{\partial\phi_1}\right)+\phi_2\nabla\left(\frac{\partial\widehat{\eta}}{\partial\phi_2}\right). \quad (4.44)$$

Multiply (4.44) by  $\theta$  and subtract this from (4.43). Using the definition of  $\mathbf{g}_1$  and  $\mathbf{g}_2$  in (4.39), we have

$$\mathbf{g}_1+\mathbf{g}_2=-\left(\frac{\partial\widehat{\varepsilon}}{\partial\theta}-\theta\frac{\partial\widehat{\eta}}{\partial\theta}\right)\nabla\theta. \quad (4.45)$$

The right hand side vanishes by (4.38).

Thus, the net entropy production of a small volume in the gel can be simply written by

$$Q=\frac{1}{\theta}(\mathbf{v}_1-\mathbf{v}_2)\cdot(\mathbf{g}_1-\mathbf{f}_1)+\frac{1}{\theta}((\nabla\mathbf{v}_1):(\mathcal{T}_1-\mathcal{T}_1^{\text{elas}})+(\nabla\mathbf{v}_2):\mathcal{T}_2)-\frac{1}{\theta^2}(\mathbf{q}\cdot\nabla\theta).$$

In a completely similar way, we get

$$\begin{aligned} Q_f &= \frac{\partial\eta_f}{\partial t} + \nabla\cdot(\eta_f\mathbf{v}_f) + \nabla\cdot\left(\frac{\mathbf{q}_f}{\theta_f}\right) \\ &= \frac{\partial\eta_f}{\partial\theta_f}\frac{\partial\theta_f}{\partial t} + \nabla\cdot(\eta_f\mathbf{v}_f) + \nabla\cdot\left(\frac{\mathbf{q}_f}{\theta_f}\right) \\ &= \frac{1}{\theta_f}\frac{\partial\widehat{\varepsilon}}{\partial\theta_f}\frac{\partial\theta_f}{\partial t} + \nabla\cdot(\eta_f\mathbf{v}_f) + \nabla\cdot\left(\frac{\mathbf{q}_f}{\theta_f}\right) \\ &= \frac{1}{\theta_f}C_{fv}\frac{\partial\theta_f}{\partial t} + \nabla\cdot(\eta_f\mathbf{v}_f) + \nabla\cdot\left(\frac{\mathbf{q}_f}{\theta_f}\right) \\ &= \frac{1}{\theta_f}\left(\mathcal{T}_f:\nabla\mathbf{v}_f - \mathbf{v}_f\cdot\nabla\varepsilon_f - \nabla\cdot\mathbf{q}_f\right) + \nabla\cdot(\eta_f\mathbf{v}_f) + \nabla\cdot\left(\frac{\mathbf{q}_f}{\theta_f}\right), \end{aligned} \quad (4.46)$$

where (4.36) is used in the last equality.

Note that

$$\frac{1}{\theta_f}(\mathbf{v}_f\cdot\nabla\varepsilon_f) = \frac{1}{\theta_f}\mathbf{v}_f\cdot\left(\frac{\partial\varepsilon_f}{\partial\theta_f}\nabla\theta_f\right) = \mathbf{v}_f\cdot\left(\frac{\partial\eta_f}{\partial\theta_f}\nabla\theta_f\right) = \mathbf{v}_f\cdot\nabla\eta_f,$$

because of (4.38) and the fact that  $\varepsilon_f$  is a function of  $\theta_f$  only. By use of this identity and (3.8), (4.46) can be written as

$$Q_f = \frac{1}{\theta_f} (\mathcal{T}_f : \nabla \mathbf{v}_f) - \frac{1}{\theta_f^2} (\mathbf{q}_f \cdot \nabla \theta_f).$$

Therefore, we have the following relations so that the non-negativity of the net entropy production density, referred to as the local version of the second law of thermodynamics, is satisfied for any choices  $\{\phi_1, \mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_f, \theta, \theta_f\}$ :

$$\begin{aligned} \mathbf{f}_1 &= \mathbf{g}_1 - \kappa(\mathbf{v}_1 - \mathbf{v}_2), \\ \mathbf{f}_2 &= \mathbf{g}_2 - \kappa(\mathbf{v}_2 - \mathbf{v}_1) = -\mathbf{f}_1, \\ \mathbf{q} &= -\lambda \nabla \theta, \\ \mathbf{q}_f &= -\lambda_f \nabla \theta_f, \end{aligned} \tag{4.47}$$

in which  $\kappa$  is the friction coefficient, and  $\lambda, \lambda_f$  are the heat conductance. Those coefficients are positive and  $\kappa, \lambda$  may depend on the volume fraction  $\phi_1$  of polymer networks.

On applying all these restrictions (4.47) to (4.34) and (4.36), we are led to the evolution equations of a thermoelastic gel and surrounding fluid of the form:

$$\begin{aligned} C_v \frac{\partial \theta}{\partial t} &= \kappa |\mathbf{v}_1 - \mathbf{v}_2|^2 + \mu_1 |\nabla_S \mathbf{v}_1|^2 + \mu_2 |\nabla_S \mathbf{v}_2|^2 + \nabla \cdot (\lambda \nabla \theta) \\ &\quad - \theta \left( \phi_1 \mathbf{v}_1 \cdot \nabla \left( \frac{\partial \hat{\eta}}{\partial \phi_1} \right) + \phi_2 \mathbf{v}_2 \cdot \nabla \left( \frac{\partial \hat{\eta}}{\partial \phi_2} \right) \right) \\ &\quad + \theta \mathbf{v}_1 \cdot \left( \frac{1}{3\phi_1} \nabla \phi_1 \left( \frac{\partial \eta}{\partial \mathcal{F}} : \mathcal{F} \right) + \frac{\partial \eta}{\partial \mathcal{F}} : \nabla \mathcal{F} \right) \\ &\quad + \theta (\nabla \mathbf{v}_1) : \left( \frac{1}{3} \left( \frac{\partial \eta}{\partial \mathcal{F}} : \mathcal{F} \right) \mathbf{I} - \frac{\partial \eta}{\partial \mathcal{F}} \mathcal{F}^T \right) \end{aligned} \tag{4.48}$$

and

$$C_{fv} \frac{\partial \theta_f}{\partial t} = \mu_f |\nabla_S \mathbf{v}_f|^2 - \mathbf{v}_f \cdot \nabla \varepsilon_f + \nabla \cdot (\lambda_f \nabla \theta_f). \tag{4.49}$$

We end this section with the following proposition that summarizes the results.

**Proposition 4.4.1.** *Suppose that the balance laws of mass (3.3), linear momentum (3.5)-(3.7), and energy (4.2)-(4.3) and the constraint (3.2) hold. Given the thermodynamic relations (4.16), suppose that the entropy inequality holds for all processes  $\{\phi_1, \mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_f, \theta, \theta_f\}$ . Then the constitutive restrictions (4.39) and (4.47) hold.*

## 4.5 Galilean Invariance

In this section, we prove the Galilean invariance of equations in the motion of the gel. Let  $(\bar{\mathbf{x}}, \bar{t})$  be a pair of position and time in another inertial frame, say  $\bar{\mathcal{S}}$ , whose motion is supposed to be uniform with a constant velocity  $\mathbf{v}_c$  relative to the present frame of reference. Let the velocities for polymer networks and fluid in the gel in  $\bar{\mathcal{S}}$  be denoted by  $\bar{\mathbf{v}}_i = \bar{\mathbf{v}}_i(\bar{\mathbf{x}}, \bar{t})$ , ( $i = 1, 2$ ), respectively. By assuming that  $\bar{t} = t$ , we have then

$$\begin{aligned}\bar{\mathbf{x}} &= \mathbf{x} - \mathbf{v}_c t, \\ \bar{\mathbf{v}}_1(\bar{\mathbf{x}}, t) &= \mathbf{v}_1(\mathbf{x}, t) - \mathbf{v}_c, \\ \bar{\mathbf{v}}_2(\bar{\mathbf{x}}, t) &= \mathbf{v}_2(\mathbf{x}, t) - \mathbf{v}_c.\end{aligned}\tag{4.50}$$

Easy calculus shows that for any scalar function  $f$ ,

$$\bar{\nabla} f = \nabla f, \quad \frac{\partial f}{\partial \bar{t}} = \mathbf{v}_c \cdot \nabla f + \frac{\partial f}{\partial t},$$

and accordingly,

$$\bar{\nabla} \cdot \bar{\mathbf{v}}_i = \nabla \cdot \mathbf{v}_i, \quad \bar{\nabla} \bar{\mathbf{v}}_i = \nabla \mathbf{v}_i,$$

from which we can easily see that equations (3.2), (3.4) and (3.5) hold in  $\bar{\mathcal{S}}$ . Here  $\bar{\nabla}$  has been used to represent the gradient notation in  $\bar{\mathcal{S}}$ .

As for the evolution equation for temperature (4.48), since

$$C_v \frac{\partial \theta}{\partial \bar{t}} = C_v \frac{\partial \theta}{\partial t} + C_v \mathbf{v}_c \cdot \nabla \theta$$

and

$$\begin{aligned}
& \kappa|\bar{\mathbf{v}}_1 - \bar{\mathbf{v}}_2|^2 + \mu_1|\bar{\nabla}_S \bar{\mathbf{v}}_1|^2 + \mu_2|\bar{\nabla}_S \bar{\mathbf{v}}_2|^2 + \bar{\nabla} \cdot (\lambda \bar{\nabla} \theta) - \theta \left( \phi_1 \bar{\mathbf{v}}_1 \cdot \bar{\nabla} \left( \frac{\partial \hat{\eta}}{\partial \phi_1} \right) + \phi_2 \bar{\mathbf{v}}_2 \cdot \bar{\nabla} \left( \frac{\partial \hat{\eta}}{\partial \phi_2} \right) \right) \\
& + \theta \bar{\mathbf{v}}_1 \cdot \left( \frac{1}{3\phi_1} \bar{\nabla} \phi_1 \left( \frac{\partial \eta}{\partial \bar{\mathcal{F}}} : \bar{\mathcal{F}} \right) + \frac{\partial \eta}{\partial \bar{\mathcal{F}}} : \bar{\nabla} \bar{\mathcal{F}} \right) + \theta (\bar{\nabla} \bar{\mathbf{v}}_1) : \left( \frac{1}{3} \left( \frac{\partial \eta}{\partial \bar{\mathcal{F}}} : \bar{\mathcal{F}} \right) \mathbf{I} - \frac{\partial \eta}{\partial \bar{\mathcal{F}}} \bar{\mathcal{F}}^T \right) \\
= & \kappa|\mathbf{v}_1 - \mathbf{v}_2|^2 + \mu_1|\nabla_S \mathbf{v}_1|^2 + \mu_2|\nabla_S \mathbf{v}_2|^2 + \nabla \cdot (\lambda \nabla \theta) \\
& - \theta \left( \phi_1 (\mathbf{v}_1 - \mathbf{v}_c) \cdot \nabla \left( \frac{\partial \hat{\eta}}{\partial \phi_1} \right) + \phi_2 (\mathbf{v}_2 - \mathbf{v}_c) \cdot \nabla \left( \frac{\partial \hat{\eta}}{\partial \phi_2} \right) \right) \\
& + \theta (\mathbf{v}_1 - \mathbf{v}_c) \cdot \left( \frac{1}{3\phi_1} \nabla \phi_1 \left( \frac{\partial \eta}{\partial \mathcal{F}} : \mathcal{F} \right) + \frac{\partial \eta}{\partial \mathcal{F}} : \nabla \mathcal{F} \right) + \theta (\nabla \mathbf{v}_1) : \left( \frac{1}{3} \left( \frac{\partial \eta}{\partial \mathcal{F}} : \mathcal{F} \right) \mathbf{I} - \frac{\partial \eta}{\partial \mathcal{F}} \mathcal{F}^T \right),
\end{aligned}$$

in order for (4.48) to be invariant under Galilean transformation, it should be satisfied that

$$C_v \nabla \theta = \theta \left( \phi_1 \nabla \left( \frac{\partial \hat{\eta}}{\partial \phi_1} \right) + \phi_2 \nabla \left( \frac{\partial \hat{\eta}}{\partial \phi_2} \right) - \frac{1}{3\phi_1} \nabla \phi_1 \left( \frac{\partial \eta}{\partial \mathcal{F}} : \mathcal{F} \right) - \frac{\partial \eta}{\partial \mathcal{F}} : \nabla \mathcal{F} \right).$$

From  $C_v = \frac{\partial \hat{\varepsilon}}{\partial \theta} = \theta \frac{\partial \hat{\eta}}{\partial \theta}$ , we need only show that

$$\frac{\partial \hat{\eta}}{\partial \theta} \nabla \theta = \phi_1 \nabla \left( \frac{\partial \hat{\eta}}{\partial \phi_1} \right) + \phi_2 \nabla \left( \frac{\partial \hat{\eta}}{\partial \phi_2} \right) - \frac{1}{3\phi_1} \nabla \phi_1 \left( \frac{\partial \eta}{\partial \mathcal{F}} : \mathcal{F} \right) - \frac{\partial \eta}{\partial \mathcal{F}} : \nabla \mathcal{F}. \quad (4.51)$$

It is clearly true due to (4.44).

Same argument applies to equations in  $\mathcal{R}_t$ , therefore, we conclude that the governing equations in both the gel and its environment fluid are the same in any inertial frame of reference.

## Chapter 5

# Gels in One-dimensional Geometry

We restrict all the equations that we have derived in the preceding chapter to one spatial dimension. When elaborating a numerical scheme, the use of spatial description can involve difficulties because of moving interfaces of the gel. Thus, we carry out the spatial to referential transformation, and build a numerical algorithm.

### 5.1 Governing Equations in One-Dimensional Space

We consider the thermoelastic motion of a one-dimensional gel with Dirichlet boundary conditions. Let  $\mathbb{U} = [0, 1] \subset \mathbb{R}$  be the region containing the gel and fluid, and we express the domain of polymer networks at time  $t$  as  $\Omega_t = (L_\ell(t), L_r(t))$ ,  $0 < L_\ell(t) < L_r(t) < 1$ , and  $\Omega_0 = (L_\ell(0), L_r(0))$  for the reference domain. The boundaries  $L_i(t)$  move with velocities  $v_1(L_i, t)$ , ( $i = \ell, r$ ).

We assume that the velocity of surrounding fluid is zero at the ends  $x = 0, 1$ , that is,  $v_f = 0$  at  $x = 0, 1$ . Furthermore, we specify temperature values at both ends:

$$\theta_f = \theta_0 \quad \text{at } x = 0, \quad \theta_f = \theta_1 \quad \text{at } x = 1.$$

The deformation gradient is a positive number:

$$\mathcal{F} = \frac{\partial \varphi}{\partial x} := \alpha, \quad \alpha > 0,$$

and by the relation  $\phi_1 \det \mathcal{F} = \phi_{\text{ref}}$ , it is proportional to the inverse of  $\phi_1$ :

$$\alpha = \frac{\phi_{\text{ref}}}{\phi_1}, \quad \phi_{\text{ref}} = \phi_1(x, 0). \quad (5.1)$$

We let the total free energy densities at each point in  $\Omega_t$  and  $\mathcal{R}_t$ , respectively, be of the form

$$\psi = k_B (a(\theta)\phi_1 \ln \phi_1 + b(\theta)\phi_2 \ln \phi_2 + \chi(\theta)\phi_1\phi_2) - c\theta \ln \theta + \phi_1 W_{\text{elas}}(\mathcal{F}), \quad (5.2)$$

$$\psi_f = -c_f \theta_f \ln \theta_f, \quad (5.3)$$

where  $k_B$  is the Boltzmann constant,  $a(\theta)$ ,  $b(\theta)$  and the Flory-Huggins interaction parameter,  $\chi(\theta)$ , are linear functions of  $\theta$ ,  $W_{\text{elas}}(\mathcal{F})$  represents the elastic stored energy function, and  $c, c_f$  are positive constants.

Because of (5.1), we can view the elastic energy,  $W_{\text{elas}}$ , as a function of  $\phi_1$ , and thus we can write (5.2) in the form

$$\psi = k_B (a(\theta)\phi_1 \ln \phi_1 + b(\theta)\phi_2 \ln \phi_2 + \chi(\theta)\phi_1\phi_2) - c\theta \ln \theta + \phi_1 W_{\text{elas}}(\phi_1). \quad (5.4)$$

Also, by (4.27), we have

$$\begin{aligned} \widehat{\psi}(\phi_1, \phi_2, \theta) = & k_B \left[ a(\theta)\phi_1 \ln \left( \frac{\phi_1}{\phi_1 + \phi_2} \right) + b(\theta)\phi_2 \ln \left( \frac{\phi_2}{\phi_1 + \phi_2} \right) + \chi(\theta) \frac{\phi_1\phi_2}{\phi_1 + \phi_2} \right] \\ & - (\phi_1 + \phi_2)c\theta \ln \theta + \phi_1 W_{\text{elas}} \left( \frac{\phi_1}{\phi_1 + \phi_2} \right). \end{aligned}$$

From the thermodynamic relation  $\widehat{\eta} = -\partial \widehat{\psi} / \partial \theta$ , entropy density function is given by

$$\begin{aligned} \widehat{\eta} = & -k_B \left[ a'(\theta)\phi_1 \ln \left( \frac{\phi_1}{\phi_1 + \phi_2} \right) + b'(\theta)\phi_2 \ln \left( \frac{\phi_2}{\phi_1 + \phi_2} \right) + \chi'(\theta) \frac{\phi_1\phi_2}{\phi_1 + \phi_2} \right] \\ & + (\phi_1 + \phi_2)c(\ln \theta + 1), \end{aligned}$$

where we have used the prime notation to denote the derivatives over  $\theta$ .

In a similar fashion, we get

$$\eta_f = c_f (\ln \theta_f + 1).$$



The constant  $c$  has the same value as heat capacity  $C_v$ :

$$C_v = c,$$

since

$$C_v = \frac{\partial \widehat{\varepsilon}}{\partial \theta} = \frac{\partial}{\partial \theta}(\widehat{\psi} + \theta \widehat{\eta}) = \frac{\partial}{\partial \theta} \left( \widehat{\psi} - \theta \frac{\partial \widehat{\psi}}{\partial \theta} \right) = -\theta \frac{\partial^2 \widehat{\psi}}{\partial \theta^2} = \theta \frac{\partial \widehat{\eta}}{\partial \theta} = c.$$

By the same reasoning, we obtain also  $C_{f_v} = c_f$ .

Further, the associated values are given by

$$\begin{aligned} \mathcal{T}_1^{\text{elas}} &= 0, & \mathcal{T}_i^{\text{visc}} &= \mu_i v_{ix}, \quad (i = 1, 2, f), \\ \mathbf{f}_1 &= f_1 = g_1 - \kappa(v_1 - v_2), \\ g_1 &= -g_2 = \phi_2 \left( \left( \frac{\partial \widehat{\varepsilon}}{\partial \phi_2} \right)_x - \theta \left( \frac{\partial \widehat{\eta}}{\partial \phi_2} \right)_x \right) = \phi_2 \left( \left( \frac{\partial \widehat{\psi}}{\partial \phi_2} \right)_x + \theta_x \frac{\partial \widehat{\eta}}{\partial \phi_2} \right). \end{aligned}$$

For simple notation, we have used subscripts to indicate a partial differentiation.

Therefore, from (3.2)-(3.5) and (4.48) it follows that in  $\Omega_t = (L_\ell(t), L_r(t))$ ,

$$\phi_1 + \phi_2 = 1, \tag{5.5}$$

$$\frac{\partial \phi_1}{\partial t} + (\phi_1 v_1)_x = 0, \tag{5.6}$$

$$(\phi_1 v_1 + \phi_2 v_2)_x = 0, \tag{5.7}$$

$$\mu_1 v_{1xx} - \phi_1 p_x + f_1 = 0, \tag{5.8}$$

$$\mu_2 v_{2xx} - \phi_2 p_x + f_2 = 0, \tag{5.9}$$

$$\begin{aligned} C_v \frac{\partial \theta}{\partial t} &= \kappa(v_1 - v_2)^2 + \mu_1(v_{1x})^2 + \mu_2(v_{2x})^2 + \lambda \theta_{xx} \\ &\quad - \theta \left( \phi_1 v_1 \left( \frac{\partial \widehat{\eta}}{\partial \phi_1} \right)_x + \phi_2 v_2 \left( \frac{\partial \widehat{\eta}}{\partial \phi_2} \right)_x \right) \\ &= \kappa(v_1 - v_2)^2 + \mu_1(v_{1x})^2 + \mu_2(v_{2x})^2 + \lambda \theta_{xx} \\ &\quad + \theta k_B \phi_{1x} (v_1 - v_2) (a'(\theta) \phi_2 + b'(\theta) \phi_1 - 2\chi'(\theta) \phi_1 \phi_2) \\ &\quad - c \theta_x (\phi_1 v_1 + \phi_2 v_2), \end{aligned} \tag{5.10}$$

and from (3.8), (3.7), (4.49), we obtain that in  $\mathcal{R}_t = (0, L_\ell(t)) \cup (L_r(t), 1)$ ,

$$(v_f)_x = 0, \quad (5.11)$$

$$\mu_f v_{f_{xx}} - p_{f_x} = 0, \quad (5.12)$$

$$C_{fv} \frac{\partial \theta_f}{\partial t} = \mu_f (v_{f_x})^2 - c_f \theta_{f_x} v_f + \lambda_f \theta_{f_{xx}}, \quad (5.13)$$

where we have assumed  $\lambda$  and  $\lambda_f$  are constants.

The equations for boundaries (3.9)-(3.11),(4.4),(4.12) yield at  $x = L_\ell(t)$ ,

$$v_1 - v_f = (1 - \phi_1)(v_1 - v_2) = w, \quad (5.14)$$

$$(v_f - v_1)_\parallel = (v_2 - v_1)_\parallel \equiv r = 0, \quad (5.15)$$

$$\mu_f v_{f_x} - \mu_2 v_{2x} - \mu_1 v_{1x} + [p] = 0, \quad (5.16)$$

$$(\varepsilon_f - \varepsilon_2 - [p])w + \frac{(\mu_2 v_{2x})}{\phi_2} w - \mu_f v_{f_x} w + (\lambda_f \theta_{f_x} - \lambda \theta_x) = 0, \quad (5.17)$$

$$\mu_\perp w = \mu_f v_{f_x} - \frac{1}{\phi_2} \mu_2 v_{2x} + [p] + (\psi_2 - \psi_f), \quad (5.18)$$

at  $x = L_r(t)$ ,

$$v_f - v_1 = (1 - \phi_1)(v_2 - v_1) = \tilde{w}, \quad (5.19)$$

$$(v_f - v_1)_\parallel = (v_2 - v_1)_\parallel \equiv r = 0, \quad (5.20)$$

$$\mu_f v_{f_x} - \mu_2 v_{2x} - \mu_1 v_{1x} + [p] = 0, \quad (5.21)$$

$$(\varepsilon_f - \varepsilon_2 - [p])\tilde{w} + \frac{(\mu_2 v_{2x})}{\phi_2} \tilde{w} - \mu_f v_{f_x} \tilde{w} + (\lambda \theta_x - \lambda_f \theta_{f_x}) = 0, \quad (5.22)$$

$$\mu_\perp \tilde{w} = \mu_f v_{f_x} - \frac{1}{\phi_2} \mu_2 v_{2x} + [p] + (\psi_2 - \psi_f). \quad (5.23)$$

We note that the interfaces,  $x = L_i(t)$ , move with velocities  $v_1(L_i, t)$ , ( $i = \ell, r$ ), respectively. In addition,

$$\theta = \theta_f, \quad \text{at } x = L_\ell(t), L_r(t), \quad (5.24)$$

and

$$v_f = 0, \quad \theta_f = \theta_0 \quad \text{at } x = 0, \quad (5.25)$$

$$v_f = 0, \quad \theta_f = \theta_1 \quad \text{at } x = 1. \quad (5.26)$$

From (5.11) and (5.25)-(5.26), we find  $v_f \equiv 0$  in  $\mathcal{R}_t$ , so it follows from (5.12), that  $p_f$  is constant. Now, we set  $p_f = 0$  in  $(L_r(t), 1)$  for simplicity. Moreover, along with (5.5) and (5.7), both equations (5.14) and (5.19) imply that in  $\Omega_t$ ,

$$\phi_1 v_1 + \phi_2 v_2 = 0 \quad \text{or} \quad v_2 = -\frac{\phi_1 v_1}{1 - \phi_1}. \quad (5.27)$$

Adding (5.8) and (5.9), we have

$$p_x = \mu_1 v_{1xx} + \mu_2 v_{2xx}.$$

Integrating on  $x$  gives

$$p = \mu_1 v_{1x} + \mu_2 v_{2x} + k(t).$$

By comparing with (5.16) and (5.21),  $k(t) \equiv p_f = \text{constant}$  in  $(0, L_\ell(t))$  and  $k(t) \equiv 0$  in  $(L_r(t), 1)$ . Then, (5.8) can be rewritten by

$$(1 - \phi_1)\mu_1 v_{1xx} - \phi_1 \mu_2 v_{2xx} = \kappa(v_1 - v_2) - g_1.$$

Therefore, by use of (5.27), we have the following governing equations for  $\{\phi_1, v_1, \theta, \theta_f\}$  : in  $\Omega_t = (L_\ell(t), L_r(t))$ ,

$$\frac{\partial \phi_1}{\partial t} + (\phi_1 v_1)_x = 0, \quad (5.28)$$

$$(1 - \phi_1)\mu_1 v_{1xx} + \phi_1 \mu_2 \left( \frac{\phi_1 v_1}{1 - \phi_1} \right)_{xx} = \frac{\kappa}{1 - \phi_1} v_1 - g_1, \quad (5.29)$$

$$C_v \frac{\partial \theta}{\partial t} = \frac{\kappa}{(1 - \phi_1)^2} v_1^2 + \mu_1 (v_{1x})^2 + \mu_2 \left[ \left( \frac{\phi_1 v_1}{1 - \phi_1} \right)_x \right]^2 + \lambda \theta_{xx} \quad (5.30)$$

$$+ k_B \theta v_1 \phi_{1x} \left( a'(\theta) + \frac{\phi_1}{1 - \phi_1} b'(\theta) - 2\phi_1 \chi'(\theta) \right),$$

where

$$g_1 = \phi_{1x} \left[ k_B \left( -a(\theta)(1 - \phi_1) - b(\theta)\phi_1 + 2\chi(\theta)\phi_1(1 - \phi_1) \right) - \phi_1(1 - \phi_1) \left( 2W'_{\text{elas}}(\phi_1) + \phi_1 W''_{\text{elas}}(\phi_1) \right) \right].$$

Equations for the interfaces and surrounding fluid are given by  
at  $x = L_\ell(t)$ ,

$$\mu_\perp v_1 = \mu_1 v_{1x} + \mu_2 \frac{\phi_1}{(1-\phi_1)} \left( \frac{\phi_1 v_1}{1-\phi_1} \right)_x + (\psi_2 - \psi_f), \quad (5.31)$$

$$(\varepsilon_2 - \varepsilon_f + p - p_f)v_1 + \frac{\mu_2}{(1-\phi_1)} v_1 \left( \frac{\phi_1 v_1}{1-\phi_1} \right)_x + \lambda \theta_x - \lambda_f \theta_{fx} = 0, \quad (5.32)$$

$$\theta = \theta_f, \quad (5.33)$$

at  $L_r(t)$ ,

$$-\mu_\perp v_1 = \mu_1 v_{1x} + \mu_2 \frac{\phi_1}{(1-\phi_1)} \left( \frac{\phi_1 v_1}{1-\phi_1} \right)_x + (\psi_2 - \psi_f), \quad (5.34)$$

$$(\varepsilon_2 - \varepsilon_f + p)v_1 + \frac{\mu_2}{(1-\phi_1)} v_1 \left( \frac{\phi_1 v_1}{1-\phi_1} \right)_x + \lambda \theta_x - \lambda_f \theta_{fx} = 0, \quad (5.35)$$

$$\theta = \theta_f, \quad (5.36)$$

where

$$\begin{aligned} \psi_2 - \psi_f &= k_B \left\{ (b(\theta) - a(\theta))\phi_1 + b(\theta) \ln(1 - \phi_1) + \phi_1^2 \chi(\theta) \right\} + (c_f - c)\theta \ln \theta - \phi_1^2 W'_{\text{elas}}(\phi_1), \\ \varepsilon_2 - \varepsilon_f &= k_B \left\{ (b(\theta) - a(\theta))\phi_1 + b(\theta) \ln(1 - \phi_1) + \phi_1^2 \chi(\theta) \right\} - (c_f - c)\theta - \phi_1^2 W'_{\text{elas}}(\phi_1) \\ &\quad - \theta k_B \left\{ (b'(\theta) - a'(\theta))\phi_1 + b'(\theta) \ln(1 - \phi_1) + \phi_1^2 \chi'(\theta) \right\}, \end{aligned}$$

in  $\mathcal{R}_t = (0, L_\ell(t)) \cup (L_r(t), 1)$ ,

$$C_{fv} \frac{\partial \theta_f}{\partial t} = \lambda_f \theta_{fxx}, \quad (5.37)$$

and at each end of the system,

$$\theta_f = \theta_0 \quad \text{at } x = 0, \quad \theta_f = \theta_1 \quad \text{at } x = 1. \quad (5.38)$$

## 5.2 Referential Form for the Equations of Gels

In developing a numerical method for the spatially one-dimensional model, moving boundaries of the gel can be a major obstacle to using the Eulerian description. To

cope with the problem, we adopt the Lagrangian approach in which each material particles are identified and tracked. We discretize the gel using a Lagrangian mesh so that the Lagrangian nodes move at the polymer network velocity  $v_1$ . The grid is extended to the surrounding fluid domain as will be described below. For that reason, we now rewrite the governing equations in the Lagrangian frame.

Let the material description for the functions be expressed as

$$\begin{aligned} x &= \varphi(X, t), \quad X \in \Omega_0 = (L_\ell(0), L_r(0)), \\ F &= \frac{\partial \varphi}{\partial X} = \alpha > 0, \quad \alpha = \alpha(X, t), \\ V_1(X, t) &= v_1(\varphi(X, t), t), \\ \Phi(X, t) &= \phi_1(\varphi(X, t), t), \quad \Phi^0(X) = \phi_{\text{ref}}(\varphi(X, 0), 0), \\ \Theta(X, t) &= \theta(\varphi(X, t), t), \\ H(\Phi, t) &= W_{\text{elas}}(\Phi(X, t)), \end{aligned}$$

and

$$\tilde{\Theta}(X, t) = \theta_f(X, t), \quad \text{for } X \in \mathcal{R}_0.$$

We make a Eulerian to the Lagrangian transformation, in particular,

$$\begin{aligned} v_x &= \frac{\partial v}{\partial x} = \frac{\partial v}{\partial X} \frac{\partial X}{\partial x} = \frac{\partial v}{\partial X} F^{-1} = \frac{1}{\alpha} \frac{\partial V}{\partial X}, \\ v_{xx} &= \frac{\partial}{\partial x} \left( \frac{\partial v}{\partial x} \right) = \frac{\partial}{\partial X} \left( \frac{1}{\alpha} \frac{\partial V}{\partial X} \right) \frac{\partial X}{\partial x} = \frac{1}{\alpha} \frac{\partial}{\partial X} \left( \frac{1}{\alpha} \frac{\partial V}{\partial X} \right), \\ \theta_t(x, t) &= \dot{\theta}(x, t) - \theta_x(x, t) v_1(x, t) \\ &= \left[ \frac{\partial}{\partial t} \Big|_X \theta(\varphi(X, t), t) \right]_{X=\varphi^{-1}(x, t)} - \frac{\partial}{\partial X} \theta(\varphi(X, t), t) \cdot \frac{1}{\alpha} v_1(\varphi(X, t), t) \\ &= \frac{\partial \Theta}{\partial t}(X, t) - \frac{1}{\alpha} \frac{\partial \Theta}{\partial X}(X, t) V(X, t). \end{aligned}$$

Here the notation  $\frac{\partial}{\partial t} \Big|_X$  represents the partial derivative with respect to  $t$  holding  $X$  fixed.

Letting linear functions  $a(\theta)$ ,  $b(\theta)$ , and  $\chi(\theta)$  be the following form

$$a(\theta) = a_1\theta + a_0,$$

$$b(\theta) = b_1\theta + b_0,$$

$$\chi(\theta) = z_1\theta + z_0,$$

we arrive at the following equations in the referential coordinates in  $\Omega_t$ :

$$\Phi V_1 + \Phi_2 V_2 = 0, \quad (5.39)$$

$$\frac{\mu_1}{\alpha} \frac{\partial}{\partial X} \left( \frac{1}{\alpha} \frac{\partial V_1}{\partial X} \right) - \frac{\Phi}{\alpha} \frac{\partial P}{\partial X} + F_1 = 0, \quad (5.40)$$

$$\frac{\mu_2}{\alpha} \frac{\partial}{\partial X} \left( \frac{1}{\alpha} \frac{\partial V_2}{\partial X} \right) - \frac{\Phi_2}{\alpha} \frac{\partial P}{\partial X} + F_2 = 0, \quad (5.41)$$

$$\begin{aligned} C_v \frac{\partial \Theta}{\partial t} &= \kappa(V_1 - V_2)^2 + \frac{\mu_1}{\alpha^2} \left( \frac{\partial V_1}{\partial X} \right)^2 + \frac{\mu_2}{\alpha^2} \left( \frac{\partial V_2}{\partial X} \right)^2 + \frac{\lambda}{\alpha} \frac{\partial}{\partial X} \left( \frac{1}{\alpha} \frac{\partial \Theta}{\partial X} \right) \\ &\quad + k_B \frac{\Theta}{\alpha} (V_1 - V_2) \left[ a_1(1 - \Phi) + b_1\Phi - 2z_1\Phi(1 - \Phi) \right] \frac{\partial \Phi}{\partial X} \\ &\quad + \frac{C_v}{\alpha} \frac{\partial \Theta}{\partial X} (1 - \Phi)(V_1 - V_2), \end{aligned} \quad (5.42)$$

where  $\Phi_2 = 1 - \Phi$ ,  $F_2(X, t) = -F_1(X, t)$ , and

$$\begin{aligned} F_1(X, t) &= -\kappa(V_1 - V_2) - \frac{1}{\alpha} \frac{\partial \Phi}{\partial X} \left[ k_B \left( a_1(1 - \Phi) + b_1\Phi - 2z_1\Phi(1 - \Phi) \right) \Theta \right. \\ &\quad \left. + k_B \left( a_0(1 - \Phi) + b_0\Phi - 2z_0\Phi(1 - \Phi) \right) \right. \\ &\quad \left. + \Phi(1 - \Phi) \left( 2 \frac{\partial H}{\partial \Phi} + \Phi \frac{\partial}{\partial \Phi} \left( \frac{\partial H}{\partial \Phi} \right) \right) \right]. \end{aligned}$$

Next, for the temperature  $\tilde{\Theta}$  in  $\mathcal{R}_t$ , we use a moving mesh frame. Let  $x_\ell = \varphi_t(L_\ell)$  be the position of the left boundary,  $L_\ell$ , at time  $t$ . Then, there follows

$$x = \frac{\varphi(L_\ell, t)}{L_\ell} X, \quad \text{for } X \in (0, L_\ell),$$

and

$$\begin{aligned} \frac{\partial \theta_f}{\partial t} &= \frac{\partial \theta_f}{\partial t} \Big|_X + \frac{\partial x}{\partial t} \frac{\partial \theta_f}{\partial x} = \frac{\partial \tilde{\Theta}}{\partial t} + \left( \frac{X}{L_\ell} V_1(L_\ell) \right) \frac{\partial \tilde{\Theta}}{\partial X}, \\ \frac{\partial^2 \theta_f}{\partial x^2} &= \frac{\partial}{\partial x} \left( \frac{\partial \theta_f}{\partial x} \right) = \frac{\partial}{\partial x} \left( \frac{L_\ell}{\varphi(L_\ell, t)} \frac{\partial \tilde{\Theta}}{\partial X} \right) = \left( \frac{L_\ell}{\varphi(L_\ell, t)} \right)^2 \frac{\partial^2 \tilde{\Theta}}{\partial X^2}. \end{aligned}$$

By transformation, the evolution equation of temperature for the outer fluid on the left side takes the form

$$C_{fv} \left( \frac{\partial \tilde{\Theta}}{\partial t} + V_1(L_\ell) \frac{X}{L_\ell} \frac{\partial \tilde{\Theta}}{\partial X} \right) = \lambda_f \left( \frac{L_\ell}{\varphi(L_\ell, t)} \right)^2 \frac{\partial^2 \tilde{\Theta}}{\partial X^2}.$$

In the exactly similar manner, we let  $x_r = \varphi_t(L_r)$  be the position of the right boundary,  $L_r$ , at time  $t$ . For the fluid on the right side ( $x_r, 1$ ), we have

$$x = 1 - \left( \frac{1 - \varphi(L_r, t)}{1 - L_r} \right) (1 - X), \quad \text{for } X \in (0, L_r),$$

and hence

$$C_{fv} \left( \frac{\partial \tilde{\Theta}}{\partial t} + V_1(L_r) \left( \frac{1 - X}{1 - L_r} \right) \frac{\partial \tilde{\Theta}}{\partial X} \right) = \lambda_f \left( \frac{1 - L_r}{1 - \varphi(L_r, t)} \right)^2 \frac{\partial^2 \tilde{\Theta}}{\partial X^2}.$$

The boundary conditions (5.16)-(5.18) and (5.21)-(5.23) can be expressed in the referential setting, respectively, as

$$\begin{aligned} \frac{\mu_1}{\alpha} \frac{\partial V_1}{\partial X} + \frac{\mu_2}{\alpha} \frac{\partial V_2}{\partial X} - P + P_f &= 0, \\ -\mu_\perp V_1 - \frac{\mu_2}{\alpha(1 - \Phi)} \frac{\partial V_2}{\partial X} + E + P - P_f &= 0, \\ (R + P - P_f)V_1 - \frac{\mu_2}{\alpha(1 - \Phi)} \frac{\partial V_2}{\partial X} V_1 + \frac{\lambda}{\alpha} \frac{\partial \Theta}{\partial X} - \frac{\lambda_f L_\ell}{\varphi_t(L_\ell)} \frac{\partial \tilde{\Theta}}{\partial X} &= 0, \end{aligned}$$

and

$$\begin{aligned} \frac{\mu_1}{\alpha} \frac{\partial V_1}{\partial X} + \frac{\mu_2}{\alpha} \frac{\partial V_2}{\partial X} - P &= 0, \\ \mu_\perp V_1 - \frac{\mu_2}{\alpha(1 - \Phi)} \frac{\partial V_2}{\partial X} + E + P &= 0, \\ (R + P)V_1 - \frac{\mu_2}{\alpha(1 - \Phi)} \frac{\partial V_2}{\partial X} V_1 + \frac{\lambda}{\alpha} \frac{\partial \Theta}{\partial X} - \frac{\lambda_f(1 - L_r)}{1 - \varphi_t(L_r)} \frac{\partial \tilde{\Theta}}{\partial X} &= 0, \end{aligned}$$

where  $E = \psi_2 - \psi_f$ ,  $R = \varepsilon_2 - \varepsilon_f$ , and those are computed by

$$\begin{aligned} E(X, t) &= k_B \Theta \left( (b_1 - a_1)\Phi + b_1 \ln(1 - \Phi) + z_1 \Phi^2 \right) + (c_f - c) \Theta \ln \Theta \\ &\quad + k_B \left( (b_0 - a_0)\Phi + b_0 \ln(1 - \Phi) + z_0 \Phi^2 \right) - \Phi^2 \frac{\partial H}{\partial \Phi}, \\ R(X, t) &= k_B \left( (b_0 - a_0)\Phi + b_0 \ln(1 - \Phi) + z_0 \Phi^2 \right) - (c_f - c) \Theta - \Phi^2 \frac{\partial H}{\partial \Phi}. \end{aligned}$$

In addition,

$$\tilde{\Theta}(0, t) = \theta_0, \quad \tilde{\Theta}(1, t) = \theta_1.$$

### 5.3 Numerical Algorithmn

In this section, we construct an algorithm to compute the solution of the governing equations in Lagrangian coordinates. It is a time-marching algorithm which includes Newton's method and the backward Euler method at each time step.

#### 5.3.1 Discretization

We discretize the space  $[0, 1]$  to have  $M + 1$  grid points:

$$X_0 = 0, X_1, X_2, \dots, \underbrace{X_m}_{=L_\ell}, \dots, \underbrace{X_{m+n}}_{=L_r}, \dots, X_M = 1,$$

for some integers  $m, n, M$  such that  $0 < m < m + n < M$ .

The function values by the deformation mapping and temperatures at the grid points are denoted by

$$\begin{aligned} \varphi(X_i, t) &= \varphi_i, & \Theta(X_i, t) &= \Theta_i, & (i = m, m + 1, \dots, m + n), \\ \tilde{\Theta}(X_i, t) &= \tilde{\Theta}_i, & (i \in \{1, 2, \dots, m - 1\} \cup \{m + 1, \dots, M - 1\}). \end{aligned}$$

We assume that the pressure in the gel is defined at midpoints,  $P_{j/2}$ , ( $j = 2m + 1, 2m + 3, \dots, 2(m + n) - 1$ ), and its spatial derivative at the  $k$ th point is calculated as

$$\left. \frac{\partial P}{\partial X} \right|_k \simeq \frac{P_{k+1/2} - P_{k-1/2}}{\Delta X}, \quad (k = m + 1, \dots, m + n - 1).$$

For each point  $X_i$  or  $X_{i+1/2}$  ( $i = m, \dots, m + n - 1$ ), we let the values of the deformation gradient  $\alpha$ , volume fraction  $\Phi$ , velocities  $V, W$  of the polymer and fluid,



and temperature  $\Theta$  be of the form, respectively:

$$\begin{aligned}\alpha_{i+\frac{1}{2}} &= \frac{\varphi_{i+1} - \varphi_i}{\Delta X}, & \Phi_{i+\frac{1}{2}} &= \frac{1}{\alpha_{i+\frac{1}{2}}} \Phi_{i+\frac{1}{2}}^0, \\ (V_1)_i &= \frac{\partial \varphi}{\partial t}(X_i, t) := V_i, & (V_2)_i &:= W_i, \\ V_{i+\frac{1}{2}} &= \frac{V_{i+1} + V_i}{2}, & W_{i+\frac{1}{2}} &= \frac{W_{i+1} + W_i}{2}, \\ \Theta_{i+\frac{1}{2}} &= \frac{\Theta_{i+1} + \Theta_i}{2}.\end{aligned}$$

Then  $\Phi_i$ , the volume fraction of polymer networks at a node point, is computed by taking the average of the values defined at midpoints, and  $\alpha$  at the node is determined by the relation (5.1):

$$\Phi_{i+1} = \frac{\Phi_{i+\frac{1}{2}} + \Phi_{i+1+\frac{1}{2}}}{2}, \quad \alpha_{i+1} = \frac{\Phi_{i+1}^0}{\Phi_{i+1}}, \quad (i = m, \dots, m+n-2).$$

From direct calculation

$$\begin{aligned}\frac{\partial \Phi}{\partial X}(X_i, t) &\simeq \frac{\Phi_{i+\frac{1}{2}} - \Phi_{i-\frac{1}{2}}}{\Delta X}, \\ \frac{\partial}{\partial X} \left( \frac{1}{\alpha} \frac{\partial V}{\partial X} \right) (X_i, t) &\simeq \frac{1}{\Delta X} \left[ \frac{1}{\alpha} \frac{\partial V}{\partial X} \left( X_i + \frac{\Delta X}{2} \right) - \frac{1}{\alpha} \frac{\partial V}{\partial X} \left( X_i - \frac{\Delta X}{2} \right) \right] \\ &= \frac{1}{\Delta X} \left[ \frac{1}{\alpha_{i+\frac{1}{2}}} \frac{\partial V}{\partial X} (X_{i+\frac{1}{2}}) - \frac{1}{\alpha_{i-\frac{1}{2}}} \frac{\partial V}{\partial X} (X_{i-\frac{1}{2}}) \right] \\ &= \frac{1}{\Delta X} \left[ \frac{V_{i+1} - V_i}{\varphi_{i+1} - \varphi_i} - \frac{V_i - V_{i-1}}{\varphi_i - \varphi_{i-1}} \right], \\ \frac{\partial}{\partial X} \left( \frac{1}{\alpha} \frac{\partial \Theta}{\partial X} \right) (X_i, t) &\simeq \frac{1}{\Delta X} \left[ \frac{\Theta_{i+1} - \Theta_i}{\varphi_{i+1} - \varphi_i} - \frac{\Theta_i - \Theta_{i-1}}{\varphi_i - \varphi_{i-1}} \right],\end{aligned}$$

we obtain the discretized equations as follows: for  $i = m, \dots, m+n$ ,

$$\Phi_i V_i + (1 - \Phi_i) W_i = 0, \tag{5.43}$$

for  $i = m + 1, \dots, m + n - 1$ ,

$$\frac{\mu_1}{\alpha_i} \frac{1}{\Delta X} \left[ \frac{V_{i+1} - V_i}{\varphi_{i+1} - \varphi_i} - \frac{V_i - V_{i-1}}{\varphi_i - \varphi_{i-1}} \right] - \frac{\Phi_i}{\alpha_i} \frac{(P_{i+\frac{1}{2}} - P_{i-\frac{1}{2}})}{\Delta X} + F_1(X_i) = 0, \quad (5.44)$$

$$\frac{\mu_2}{\alpha_i} \frac{1}{\Delta X} \left[ \frac{W_{i+1} - W_i}{\varphi_{i+1} - \varphi_i} - \frac{W_i - W_{i-1}}{\varphi_i - \varphi_{i-1}} \right] - \frac{(1 - \Phi_i)}{\alpha_i} \frac{(P_{i+\frac{1}{2}} - P_{i-\frac{1}{2}})}{\Delta X} + F_2(X_i) = 0, \quad (5.45)$$

$$\begin{aligned} C_v \frac{\partial \Theta}{\partial t}(X_i) &= \kappa(V_i - W_i)^2 + \frac{\mu_1}{\alpha_i^2} \left( \frac{V_{i+\frac{1}{2}} - V_{i-\frac{1}{2}}}{\Delta X} \right)^2 + \frac{\mu_2}{\alpha_i^2} \left( \frac{W_{i+\frac{1}{2}} - W_{i-\frac{1}{2}}}{\Delta X} \right)^2 \\ &+ \frac{\lambda}{\alpha_i} \frac{1}{\Delta X} \left[ \frac{\Theta_{i+1} - \Theta_i}{\varphi_{i+1} - \varphi_i} - \frac{\Theta_i - \Theta_{i-1}}{\varphi_i - \varphi_{i-1}} \right] \\ &+ \frac{C_v}{\alpha_i} \frac{\Theta_{i+\frac{1}{2}} - \Theta_{i-\frac{1}{2}}}{\Delta X} (1 - \Phi_i)(V_i - W_i) \\ &+ k_B \frac{\Theta_i}{\alpha_i} (V_i - W_i) \left[ a_1(1 - \Phi_i) + b_1\Phi_i - 2z_1\Phi_i(1 - \Phi_i) \right] \frac{\Phi_{i+\frac{1}{2}} - \Phi_{i-\frac{1}{2}}}{\Delta X}, \end{aligned} \quad (5.46)$$

where

$$\begin{aligned} F_1(X_i, t) &= -\kappa(V_i - W_i) \\ &- \frac{(\Phi_{i+\frac{1}{2}} - \Phi_{i-\frac{1}{2}})}{\alpha_i (\Delta X)} \left[ k_B (a_1(1 - \Phi_i) + b_1\Phi_i - 2z_1\Phi_i(1 - \Phi_i)) \Theta_i \right. \\ &\quad \left. + k_B (a_0(1 - \Phi_i) + b_0\Phi_i - 2z_0\Phi_i(1 - \Phi_i)) \right] \\ &+ \frac{\Phi_i(1 - \Phi_i)}{\Phi_{i+\frac{1}{2}} - \Phi_{i-\frac{1}{2}}} \left( 2 \left( H_{i+\frac{1}{2}} - H_{i-\frac{1}{2}} \right) + \Phi_i \left( \frac{H_{i+1} - H_i}{\Phi_{i+1} - \Phi_i} - \frac{H_i - H_{i-1}}{\Phi_i - \Phi_{i-1}} \right) \right) \end{aligned}$$

Since moving interfaces influence the lengths of the left and right regions that the outside fluid occupy at each time, we repartition those areas.

Let  $x_m = \varphi_t(X_m)$  be the position of the left boundary,  $X_m$ , at time  $t$ . We divide  $(0, x_m)$  into  $m$  equal intervals with the length  $\Delta X_l$ . Similarly, the fluid region on the right,  $(x_{m+n}, 1)$ , is rezoned to have  $M - m - n$  intervals of the uniform length  $\Delta X_r$ . Then application of the above rearrangement gives rise to the equations for the surrounding

fluid for  $i = 1, \dots, m - 1$ ,

$$\begin{aligned} C_{fv} \frac{\partial \tilde{\Theta}}{\partial t}(X_i) = & -C_{fv} \left( \frac{X_i}{X_m} V_m \right) \frac{\tilde{\Theta}_{i+1} - \tilde{\Theta}_i}{\Delta X_l} \\ & + \frac{\lambda_f}{(\Delta X_l)^2} \left( \frac{X_m}{\varphi(X_m, t)} \right)^2 (\tilde{\Theta}_{i-1} - 2\tilde{\Theta}_i + \tilde{\Theta}_{i+1}), \end{aligned} \quad (5.47)$$

and for  $i = m + n + 1, \dots, M - 1$ ,

$$\begin{aligned} C_{fv} \frac{\partial \tilde{\Theta}}{\partial t}(X_i) = & -C_{fv} \left( \frac{1 - X_i}{1 - X_{m+n}} V_{m+n} \right) \frac{\tilde{\Theta}_{i+1} - \tilde{\Theta}_i}{\Delta X_r} \\ & + \frac{\lambda_f}{(\Delta X_r)^2} \left( \frac{1 - X_{m+n}}{1 - \varphi(X_{m+n}, t)} \right)^2 (\tilde{\Theta}_{i-1} - 2\tilde{\Theta}_i + \tilde{\Theta}_{i+1}). \end{aligned} \quad (5.48)$$

At the interfaces  $X = X_m$  and  $X = X_{m+n}$ , by the following setting

$$\begin{aligned} \alpha_m &= \alpha_{m+1/2}, & P_m &= P_{m+1/2}, \\ \alpha_{m+n} &= \alpha_{m+n-1/2}, & P_{m+n} &= P_{m+n-1/2}, \end{aligned}$$

and

$$\begin{aligned} \Phi_m &= \frac{1}{\alpha_m} \Phi_m^0, & \Phi_{m+n} &= \frac{1}{\alpha_{m+n}} \Phi_{m+n}^0, \\ \left. \frac{\partial V}{\partial X} \right|_m &\simeq \frac{V_{m+1} - V_m}{\Delta X}, & \left. \frac{\partial V}{\partial X} \right|_{m+n} &\simeq \frac{V_{m+n} - V_{m+n-1}}{\Delta X}, \\ \left. \frac{\partial H}{\partial \Phi} \right|_m &\simeq \frac{H_{m+1/2} - H_m}{\Phi_{m+1/2} - \Phi_m}, & \left. \frac{\partial H}{\partial \Phi} \right|_{m+n} &\simeq \frac{H_{m+n} - H_{m+n-1/2}}{\Phi_{m+n} - \Phi_{m+n-1/2}}, \end{aligned}$$

the equations for the interfaces can be written as

at  $X = X_m$ ,

$$\frac{\mu_1}{\alpha_m} \left( \frac{V_{m+1} - V_m}{\Delta X} \right) + \frac{\mu_2}{\alpha_m} \left( \frac{W_{m+1} - W_m}{\Delta X} \right) - P_m + P_f = 0, \quad (5.49)$$

$$- \mu_{\perp} V_m - \frac{\mu_2}{\alpha_m (1 - \Phi_m)} \left( \frac{W_{m+1} - W_m}{\Delta X} \right) + E_m + P_m - P_f = 0, \quad (5.50)$$

$$\begin{aligned} (R_m + P_m - P_f) V_m - \frac{\mu_2 V_m}{\alpha_m (1 - \Phi_m)} \left( \frac{W_{m+1} - W_m}{\Delta X} \right) \\ + \frac{\lambda}{\alpha_m} \left( \frac{\Theta_{m+1} - \Theta_m}{\Delta X} \right) - \frac{\lambda_f X_m}{\varphi_m} \left( \frac{\Theta_m - \tilde{\Theta}_{m-1}}{\Delta X_l} \right) = 0, \end{aligned} \quad (5.51)$$

at  $X = X_{m+n}$ ,

$$\frac{\mu_1}{\alpha_{m+n}} \left( \frac{V_{m+n} - V_{m+n-1}}{\Delta X} \right) + \frac{\mu_2}{\alpha_{m+n}} \left( \frac{W_{m+n} - W_{m+n-1}}{\Delta X} \right) - P_{m+n} = 0, \quad (5.52)$$

$$\mu_{\perp} V_{m+n} - \frac{\mu_2}{\alpha_{m+n}(1 - \Phi_{m+n})} \left( \frac{W_{m+n} - W_{m+n-1}}{\Delta X} \right) + E_{m+n} + P_{m+n} = 0, \quad (5.53)$$

$$\begin{aligned} & (R_{m+n} + P_{m+n})V_{m+n} - \frac{\mu_2 V_{m+n}}{\alpha_{m+n}(1 - \Phi_{m+n})} \left( \frac{W_{m+n} - W_{m+n-1}}{\Delta X} \right) \\ & + \frac{\lambda}{\alpha_{m+n}} \left( \frac{\Theta_{m+n} - \Theta_{m+n-1}}{\Delta X} \right) - \frac{\lambda_f(1 - X_{m+n})}{1 - \varphi_{m+n}} \left( \frac{\tilde{\Theta}_{m+n+1} - \Theta_{m+n}}{\Delta X_r} \right) = 0, \end{aligned} \quad (5.54)$$

where

$$\begin{aligned} E_j &= k_B \Theta_j \left( (b_1 - a_1) \Phi_j + b_1 \ln(1 - \Phi_j) + z_1 \Phi_j^2 \right) + (c_f - c) \Theta_j \ln \Theta_j \\ &+ k_B \left( (b_0 - a_0) \Phi_j + b_0 \ln(1 - \Phi_j) + z_0 \Phi_j^2 \right) - \Phi_j^2 \frac{\partial H}{\partial \Phi} \Big|_j, \\ R_j &= k_B \left( (b_0 - a_0) \Phi_j + b_0 \ln(1 - \Phi_j) + z_0 \Phi_j^2 \right) - (c_f - c) \Theta_j - \Phi_j^2 \frac{\partial H}{\partial \Phi} \Big|_j, \\ & \quad (j = m, m + n). \end{aligned}$$

The requirement that temperatures of the gel and the outer fluid are the same at the interfaces and Dirichlet conditions lead to

$$\begin{aligned} \tilde{\Theta}_m &= \Theta_m, & \tilde{\Theta}_{m+n} &= \Theta_{m+n}, \\ \tilde{\Theta}_0 &= \theta_0, & \tilde{\Theta}_M &= \theta_1. \end{aligned}$$

### 5.3.2 Algorithm

A computational algorithm for simulations is introduced in the present subsection. The algorithm designed to solve the above discrete equations consists of two parts, mechanics and temperature parts. Firstly,  $(V_i, W_i, P_{i+\frac{1}{2}})$  are computed from equations (5.43)-(5.45), (5.49)-(5.50) and (5.53) in the mechanics part. In fact, one equation at  $X_{m+n}$ , (5.52), is taken away because of its linear dependence on others, more precisely, (5.52)

results from (5.44)-(5.45) and (5.49). By this treatment, the system of equations for  $(V_i, W_i, P_{i+\frac{1}{2}})$  has the same number of equations with unknowns.

Secondly, with the values  $(V_i, W_i, P_{i+\frac{1}{2}})$ , we solve the evolution equations for temperatures  $\Theta_i$  and  $\tilde{\Theta}_j$ , ( $i \in \{m, m+1, \dots, m+n\}$ ,  $j \in \{0, 1, \dots, m\} \cup \{m+n+1, \dots, M\}$ ).

We now take a look at the algorithm step by step. Here, we take on the superscript to denote the  $n$ th time step of the iteration.

INPUT. Initial conditions:  $\varphi_i^0, \Phi_i^0$ , and  $\Theta_i^0$ .

STEP 1. Given  $n$ th time values for  $\varphi_i^n$  and  $\Theta_i^n$ , we compute  $\alpha_i^n, \Phi_i^n$ .

STEP 2. The equations (5.43)-(5.45) for  $(V_i, W_i, P_{i+\frac{1}{2}})$  are set implicitly as follows.

$$\begin{aligned} \Phi_i^n V_i^{n+1} + (1 - \Phi_i^n) W_i^{n+1} &= 0, \\ \frac{\mu_1}{\alpha_i^n} \frac{1}{\Delta X} \left[ \frac{V_{i+1}^{n+1} - V_i^{n+1}}{\varphi_{i+1}^{n+1} - \varphi_i^{n+1}} - \frac{V_i^{n+1} - V_{i-1}^{n+1}}{\varphi_i^{n+1} - \varphi_{i-1}^{n+1}} \right] - \frac{\Phi_i^n}{\alpha_i^n} \frac{(P_{i+\frac{1}{2}}^{n+1} - P_{i-\frac{1}{2}}^{n+1})}{\Delta X} + F_1^n(X_i) &= 0, \\ \frac{\mu_2}{\alpha_i^n} \frac{1}{\Delta X} \left[ \frac{W_{i+1}^{n+1} - W_i^{n+1}}{\varphi_{i+1}^{n+1} - \varphi_i^{n+1}} - \frac{W_i^{n+1} - W_{i-1}^{n+1}}{\varphi_i^{n+1} - \varphi_{i-1}^{n+1}} \right] - \frac{(1 - \Phi_i^n)}{\alpha_i^n} \frac{(P_{i+\frac{1}{2}}^{n+1} - P_{i-\frac{1}{2}}^{n+1})}{\Delta X} \\ &+ F_2^n(X_i) = 0, \end{aligned}$$

$$\begin{aligned} F_1^n(X_i, t) &= -\kappa(V_i^{n+1} - W_i^{n+1}) \\ &- \frac{k_B (\Phi_{i+\frac{1}{2}}^n - \Phi_{i-\frac{1}{2}}^n)}{\alpha_i^n (\Delta X)} \left[ \left( a_1(1 - \Phi_i^n) + b_1 \Phi_i^n - 2z_1 \Phi_i^n (1 - \Phi_i^n) \right) \Theta_i^n \right. \\ &\quad \left. + \left( a_0(1 - \Phi_i^n) + b_0 \Phi_i^n - 2z_0 \Phi_i^n (1 - \Phi_i^n) \right) \right] \\ &- \frac{\Phi_i^n (1 - \Phi_i^n)}{\alpha_i^n (\Delta X)} \left( 2 \left( H_{i+\frac{1}{2}}^n - H_{i-\frac{1}{2}}^n \right) + \Phi_i^n \left( \frac{H_{i+1}^n - H_i^n}{\Phi_{i+1}^n - \Phi_i^n} - \frac{H_i^n - H_{i-1}^n}{\Phi_i^n - \Phi_{i-1}^n} \right) \right). \end{aligned}$$

Using the relation  $\varphi_i^{n+1} = \varphi_i^n + V_i^{n+1}\Delta t$ , we can rewrite

$$\begin{aligned} & \Phi_i^n V_i^{n+1} + (1 - \Phi_i^n)W_i^{n+1} = 0, \\ & \frac{\mu_1}{\alpha_i^n} \frac{1}{\Delta X} \left[ \frac{V_{i+1}^{n+1} - V_i^{n+1}}{\varphi_{i+1}^n - \varphi_i^n + (V_{i+1}^{n+1} - V_i^{n+1})\Delta t} - \frac{V_i^{n+1} - V_{i-1}^{n+1}}{\varphi_i^n - \varphi_{i-1}^n + (V_i^{n+1} - V_{i-1}^{n+1})\Delta t} \right] \\ & \quad - \frac{\Phi_i^n}{\alpha_i^n} \frac{\left( P_{i+\frac{1}{2}}^{n+1} - P_{i-\frac{1}{2}}^{n+1} \right)}{\Delta X} + F_1^n(X_i) = 0, \\ & \frac{\mu_2}{\alpha_i^n} \frac{1}{\Delta X} \left[ \frac{W_{i+1}^{n+1} - W_i^{n+1}}{\varphi_{i+1}^n - \varphi_i^n + (V_{i+1}^{n+1} - V_i^{n+1})\Delta t} - \frac{W_i^{n+1} - W_{i-1}^{n+1}}{\varphi_i^n - \varphi_{i-1}^n + (V_i^{n+1} - V_{i-1}^{n+1})\Delta t} \right] \\ & \quad - \frac{(1 - \Phi_i^n)}{\alpha_i^n} \frac{\left( P_{i+\frac{1}{2}}^{n+1} - P_{i-\frac{1}{2}}^{n+1} \right)}{\Delta X} + F_2^n(X_i) = 0. \end{aligned}$$

In company with (5.49)-(5.50) and (5.53) of the form

$$\begin{aligned} & \frac{\mu_1}{\alpha_m^n} \left( \frac{V_{m+1}^{n+1} - V_m^{n+1}}{\Delta X} \right) + \frac{\mu_2}{\alpha_m^n} \left( \frac{W_{m+1}^{n+1} - W_m^{n+1}}{\Delta X} \right) - P_m^{n+1} + P_f = 0, \\ & -\mu_{\perp} V_m^{n+1} - \frac{\mu_2}{\alpha_m^n (1 - \Phi_m^n)} \left( \frac{W_{m+1}^{n+1} - W_m^{n+1}}{\Delta X} \right) + E_m^n + P_m^{n+1} - P_f = 0, \\ & \mu_{\perp} V_{m+n}^{n+1} - \frac{\mu_2}{\alpha_{m+n}^n (1 - \Phi_{m+n}^n)} \left( \frac{W_{m+n}^{n+1} - W_{m+n-1}^{n+1}}{\Delta X} \right) + E_{m+n}^n + P_{m+n}^{n+1} = 0, \end{aligned}$$

where

$$\begin{aligned} E_j^n &= k_B \Theta_j^n \left( (b_1 - a_1) \Phi_j^n + b_1 \ln(1 - \Phi_j^n) + z_1 (\Phi_j^n)^2 \right) + (c_f - c) \Theta_j^n \ln \Theta_j^n \\ & \quad + k_B \left( (b_0 - a_0) \Phi_j^n + b_0 \ln(1 - \Phi_j^n) + z_0 (\Phi_j^n)^2 \right) - (\Phi_j^n)^2 \frac{\partial H}{\partial \Phi} \Big|_j, \\ & \quad (j = m, m + n), \end{aligned}$$

we solve for  $(V_i^{n+1}, W_i^{n+1}, P_{i+\frac{1}{2}}^{n+1})$  this coupled nonlinear system of equations using Newton's Method.

STEP 3. With the backward Euler method, use discretized version (5.46) and the result

$(V_i^{n+1}, W_i^{n+1}, P_{i+\frac{1}{2}}^{n+1})$  obtained at STEP 2 to find  $\Theta_i^{n+1}$ :

$$\begin{aligned}
& C_v \frac{\Theta_i^{n+1} - \Theta_i^n}{\Delta t} \\
&= \kappa (V_i^{n+1} - W_i^{n+1})^2 + \frac{\mu_1 (V_{i+1}^{n+1} - V_{i-1}^{n+1})^2}{(2\alpha_i^n (\Delta X))^2} + \frac{\mu_2 (W_{i+1}^{n+1} - W_{i-1}^{n+1})^2}{(2\alpha_i^n (\Delta X))^2} \\
&+ \frac{\lambda}{\alpha_i^n} \frac{1}{\Delta X} \left[ \frac{\Theta_{i+1}^{n+1} - \Theta_i^{n+1}}{\varphi_{i+1}^n - \varphi_i^n + (V_{i+1}^{n+1} - V_i^{n+1})\Delta t} - \frac{\Theta_i^{n+1} - \Theta_{i-1}^{n+1}}{\varphi_i^n - \varphi_{i-1}^n + (V_i^{n+1} - V_{i-1}^{n+1})\Delta t} \right] \\
&+ \frac{C_v}{\alpha_i^n} \frac{\Theta_{i+1}^{n+1} - \Theta_{i-1}^{n+1}}{2\Delta X} (1 - \Phi_i^n) (V_i^{n+1} - W_i^{n+1}) \\
&+ k_B \frac{\Theta_i^{n+1}}{\alpha_i^n} (V_i^{n+1} - W_i^{n+1}) \left[ a_1 (1 - \Phi_i^n) + b_1 \Phi_i^n - 2z_1 \Phi_i^n (1 - \Phi_i^n) \right] \frac{\Phi_{i+\frac{1}{2}}^n - \Phi_{i-\frac{1}{2}}^n}{\Delta X}.
\end{aligned}$$

From (5.47) and (5.48), expressions for finding the temperature  $\tilde{\Theta}_i$  are given by, for  $i = 1, \dots, m-1$ ,

$$\begin{aligned}
C_{fv} \frac{\tilde{\Theta}_i^{n+1} - \tilde{\Theta}_i^n}{\Delta t} &= -C_{fv} \left( \frac{X_i}{X_m} V_m^{n+1} \right) \frac{\tilde{\Theta}_{i+1}^{n+1} - \tilde{\Theta}_i^{n+1}}{\Delta X_l} \\
&+ \frac{\lambda_f}{(\Delta X_l)^2} \left( \frac{X_m}{\varphi_m^n + V_m^{n+1} \Delta t} \right)^2 (\tilde{\Theta}_{i-1}^{n+1} - 2\tilde{\Theta}_i^{n+1} + \tilde{\Theta}_{i+1}^{n+1}),
\end{aligned}$$

and for  $i = m+n+1, \dots, M-1$ ,

$$\begin{aligned}
C_{fv} \frac{\tilde{\Theta}_i^{n+1} - \tilde{\Theta}_i^n}{\Delta t} &= -C_{fv} \left( \frac{1 - X_i}{1 - X_{m+n}} V_{m+n}^{n+1} \right) \frac{\tilde{\Theta}_{i+1}^{n+1} - \tilde{\Theta}_i^{n+1}}{\Delta X_r} \\
&+ \frac{\lambda_f}{(\Delta X_r)^2} \left( \frac{1 - X_{m+n}}{1 - \varphi_{m+n}^n - V_{m+n}^{n+1} \Delta t} \right)^2 (\tilde{\Theta}_{i-1}^{n+1} - 2\tilde{\Theta}_i^{n+1} + \tilde{\Theta}_{i+1}^{n+1}).
\end{aligned}$$

The equations (5.51) and (5.54) for interfaces result in

$$\begin{aligned}
& (R_m^n + P_m^{n+1} - P_f) V_m^{n+1} - \frac{\mu_2 V_m^{n+1}}{\alpha_m^n (1 - \Phi_m^n)} \left( \frac{W_{m+1}^{n+1} - W_m^{n+1}}{\Delta X} \right) \\
&+ \frac{\lambda}{\alpha_m^n} \left( \frac{\Theta_{m+1}^{n+1} - \Theta_m^{n+1}}{\Delta X} \right) - \frac{\lambda_f X_m}{(\varphi_m^n + V_m^{n+1} \Delta t)} \left( \frac{\Theta_m^{n+1} - \tilde{\Theta}_{m-1}^{n+1}}{\Delta X_l} \right) = 0,
\end{aligned}$$

$$\begin{aligned}
& (R_{m+n}^n + P_{m+n}^{n+1})V_{m+n}^{n+1} - \frac{\mu_2 V_{m+n}^{n+1}}{\alpha_{m+n}^n (1 - \Phi_{m+n}^n)} \left( \frac{W_{m+n}^{n+1} - W_{m+n-1}^{n+1}}{\Delta X} \right) \\
& + \frac{\lambda}{\alpha_{m+n}^n} \left( \frac{\Theta_{m+n}^{n+1} - \Theta_{m+n-1}^{n+1}}{\Delta X} \right) - \frac{\lambda_f (1 - X_{m+n})}{(1 - \varphi_{m+n}^n - V_{m+n}^{n+1} \Delta t)} \left( \frac{\tilde{\Theta}_{m+n+1}^{n+1} - \Theta_{m+n}^{n+1}}{\Delta X_r} \right) = 0,
\end{aligned}$$

where

$$\begin{aligned}
R_j^n = k_B \left( (b_0 - a_0) \Phi_j^n + b_0 \ln(1 - \Phi_j^n) + z_0 (\Phi_j^n)^2 \right) - (c_f - c) \Theta_j^n - (\Phi_j^n)^2 \frac{\partial H}{\partial \Phi} \Big|_j, \\
(j = m, m + n).
\end{aligned}$$

Solve for  $(\Theta^{n+1}, \tilde{\Theta}^{n+1})$ .

STEP 4. Compute  $\varphi^{n+1}$  from

$$\varphi_i^{n+1} = \varphi_i^n + V_i^{n+1} \Delta t.$$

STEP 5. Repeat this procedure.

### 5.3.3 Convergence Studies

In the present subsection, we demonstrate the convergence of the algorithm. Our strategy is that we first refine an existing mesh by a factor of two, perform the algorithm to find the solution on the finer mesh, and compute the difference of the solutions on the former and refined meshes in an appropriate norm. Next, with the refined mesh, we repeat the above procedure, and then evaluate the divided differences.

**Definition 5.3.1.** Let  $u_M$  be the numerical solution when grid size is  $\frac{1}{M}$ , and  $u$  be the exact solution to the system of partial differential equations. Then, we say that the sequence  $(u_M)$  converges to  $u$  if, given a norm  $\|\cdot\|$ , the norm of error is bounded, that is, if there exist constants  $C > 0$  and  $\gamma > 0$  such that

$$\|u_M - u\| \leq C \left( \frac{1}{M} \right)^\gamma, \quad (5.55)$$

where  $C$  is independent of  $M$ .



Here  $\gamma$  is called *the order of convergence* of the sequence  $(u_M)$ . If  $\gamma = 1$ , the sequence converges linearly, and if  $\gamma = 2$ , it is quadratically convergent. In general, larger  $\gamma$  means more rapid convergence.

We take  $N = 2^k n$ , ( $k, n \in \mathbb{N}$ ). If the sequence  $(u_N)$  behaves in a reasonable way as  $n$  varies, and if the divided differences are not greater than  $2^{-\gamma}$  approximately:

$$\frac{\|u_{2N} - u_{4N}\|}{\|u_N - u_{2N}\|} \lesssim 2^{-\gamma}, \quad (5.56)$$

then the sequence is convergent. The reason is the following.

Suppose the quantity on the left side of (5.56) is bounded by a number  $\beta$ , ( $0 < \beta < 2^{-\gamma}$ ). Then, for any  $N$ ,

$$\begin{aligned} \|u_N - u\| &\leq \sum_{k=0}^{\infty} \|u_{2^k N} - u_{2^{k+1} N}\| \\ &= \|u_N - u_{2N}\| + \|u_{2N} - u_{2^2 N}\| + \|u_{2^2 N} - u_{2^3 N}\| + \cdots \\ &\leq \|u_N - u_{2N}\| + \beta \|u_N - u_{2N}\| + \beta^2 \|u_N - u_{2N}\| + \cdots \\ &= (1 + \beta + \beta^2 + \cdots) \|u_N - u_{2N}\| \\ &= \frac{\beta}{1 - \beta} \|u_N - u_{2N}\|, \end{aligned}$$

and from which, there follows

$$\begin{aligned} \|u_{2^{\tilde{k}} N} - u\| &\leq \frac{\beta}{1 - \beta} \|u_{2^{\tilde{k}} N} - u_{2^{(\tilde{k}+1)} N}\| \\ &\leq \frac{\beta}{1 - \beta} \beta \|u_{2^{(\tilde{k}-1)} N} - u_{2^{\tilde{k}} N}\| \\ &\leq \cdots \\ &\leq \frac{\beta^{\tilde{k}+1}}{1 - \beta} \|u_N - u_{2N}\| \\ &\leq \frac{1}{(2^{\tilde{k}} N)^\gamma} \frac{N^\gamma \beta}{1 - \beta} \|u_N - u_{2N}\|, \end{aligned}$$

for any  $\tilde{k} = 0, 1, 2, \dots$ . By letting  $2^{\tilde{k}} N = M$ , we reach the desired inequality of the form (5.55).

Based upon this result, we employ the divide differences of the sequence of numerical solutions for convergence studies. We begin with the gel of  $M_0 + 1$  grid points with time

step size  $\Delta t$ . At one step for refinement, the mesh spacing is reduced by a factor of two whereas the number of nodes becomes  $M = 2M_0 + 1$ . We make the same rate of reduction in time-step size as the grid size. An approximate solution is generated on the reconstructed mesh points. In order to compute difference of the two solutions, we take on values at the coincident nodes with the previous ones. That is, the  $M_0 + 1$  nodes are located on the  $(2k + 1)$ th ( $k = 0, 1, 2, \dots, M_0$ ) place of the new mesh, and numerical values on the  $(2k + 1)$ th point are taken for the solution  $u_{2M_0}$ . In the completely same manner, we find  $u_{4M_0}$ , then calculate the ratio of the differences

$$\frac{\|u_{4M_0} - u_{2M_0}\|}{\|u_{2M_0} - u_{M_0}\|},$$

with  $L^2$  norm defined by

$$\|u_{2M} - u_M\| = \left( \sum_{i=2}^{M+1} \left| u_{2M}^{(i)} - u_M^{(i)} \right|^2 \frac{1}{M} \right)^{1/2}.$$

Here  $u_M^{(i)}$  represents the value evaluated at the node  $i$ . Continue this process to obtain more divided differences.

We performed the numerical task with the uniform gel ( $\phi_1 = 0.5, \theta = 0.5$ ) under a motion

$$\varphi(x, t) = x(t) + \frac{1}{16}x(t)^2.$$

In this computer simulation, the parameter values are chosen as

$$\begin{aligned} \mu_1 = \mu_2 = 0.01, \quad \mu_{\perp} = 1, \quad \kappa = 1, \quad k_B = 1, \\ C_v = C_{fv} = 0.5, \quad \lambda_f = \lambda = 1, \quad P_f = 0, \quad W_{\text{elas}}(\phi_1) = 0, \\ a(\theta) = 0, \quad b(\theta) = \theta, \quad \chi(\theta) = 0.3. \end{aligned}$$

We note that a discussion about parameters is taken place in the next chapter. (See Chapter 6.)

The interval length in the mesh, time step size and the number of iterations,  $(h, \Delta t, N)$ , where  $h = \frac{1}{M}$ , are applied as under.

Table 5.1: Triples of  $(h, \Delta t, N)$ 

$h$	$\Delta t$	$N$
1/10	$\Delta t_0$	$N_0$
1/20	$\Delta t_0/2$	$2N_0$
1/40	$\Delta t_0/4$	$4N_0$
1/80	$\Delta t_0/8$	$8N_0$
1/160	$\Delta t_0/16$	$16N_0$
1/320	$\Delta t_0/32$	$32N_0$

The resulting values of the divided differences of  $(\Phi, V, \Theta)$  are shown in Tables 5.2(a)-5.2(d). Each columns represent

$$DD(10) := \frac{\|u_{40} - u_{20}\|}{\|u_{20} - u_{10}\|}, \quad DD(20) := \frac{\|u_{80} - u_{40}\|}{\|u_{40} - u_{20}\|},$$

$$DD(40) := \frac{\|u_{160} - u_{80}\|}{\|u_{80} - u_{40}\|}, \quad DD(80) := \frac{\|u_{320} - u_{160}\|}{\|u_{160} - u_{80}\|}.$$

As seen in the table, the figures are approximately less than or equal to one half. Therefore, this computational outcome verifies that the algorithm we proposed is reasonable in the convergence, or rather, it is the first order scheme.

Table 5.2: Divided Differences with  $M_0 = 10$ (a)  $\Delta t_0 = 0.001, N_0 = 100$ 

$u$	$DD(10)$	$DD(20)$	$DD(40)$	$DD(80)$
$\Phi$	0.4149	0.3873	0.3844	0.3945
$V$	0.4496	0.4583	0.4744	0.4855
$\Theta$	0.5015	0.4961	0.4969	0.4982

(b)  $\Delta t_0 = 0.001, N_0 = 1000$ 

$u$	$DD(10)$	$DD(20)$	$DD(40)$	$DD(80)$
$\Phi$	0.4077	0.4378	0.4630	0.4808
$V$	0.4290	0.4622	0.4806	0.4907
$\Theta$	0.4745	0.4862	0.4929	0.4964

(c)  $\Delta t_0 = 0.01, N_0 = 100$ 

$u$	$DD(10)$	$DD(20)$	$DD(40)$	$DD(80)$
$\Phi$	0.3986	0.4288	0.4559	0.4761
$V$	0.4271	0.4611	0.4801	0.4905
$\Theta$	0.4756	0.4867	0.4932	0.4966

(d)  $\Delta t_0 = 0.01, N_0 = 500$ 

$u$	$DD(10)$	$DD(20)$	$DD(40)$	$DD(80)$
$\Phi$	0.4885	0.4932	0.4964	0.4985
$V$	0.4405	0.4688	0.4841	0.4918
$\Theta$	0.4577	0.4849	0.4961	0.4991

## Chapter 6

# Computation Results

In this chapter, we explore movement of a gel in the system under an imposed thermal gradient. In particular, it is of interest to us how parameter values influence the direction in which the gel moves. We study parameters and analytically estimate the response of travelling gel to change of parameter values. Numerical simulation follows to compare with the estimate.

### 6.1 Nondimensionalization

In order to assess which parameter is relatively more important on the system, we nondimensionalize the equations (5.5)-(5.26) by scaling all the variables. Let

$$L = \text{length}(\mathbb{U}), \quad \theta_0 < \hat{\theta} < \theta_1, \quad U = \frac{k_B \hat{\theta}}{v_0 \kappa L}, \quad \hat{P} = \kappa U L$$

( $v_0$  is the unit volume) be the typical length, temperature, velocity, and pressure, respectively, and we write

$$\begin{aligned} x &= Lx', & v_i &= Uv'_i, \quad (i = 1, 2, f), & t &= \frac{L}{U}t', \\ p &= \hat{P}p', & p_f &= \hat{P}p'_f, & \varepsilon &= \hat{P}\varepsilon', & \psi &= \hat{P}\psi', & \theta &= \hat{\theta}\theta', & \theta_f &= \hat{\theta}\theta'_f, \\ a(\theta) &= \frac{\hat{\theta}}{L^3}a'(\theta'), & b(\theta) &= \frac{\hat{\theta}}{L^3}b'(\theta'), & \chi(\theta) &= \frac{\hat{\theta}}{L^3}\chi'(\theta'). \end{aligned}$$

The primed variables have no dimension, and by substituting all these into the equations (5.5)-(5.26) and dropping the primes, we have the following dimensionless model

in  $\Omega_t$ ,

$$\phi_1 + \phi_2 = 1, \quad (6.1)$$

$$\frac{\partial \phi_1}{\partial t} + (\phi_1 v_1)_x = 0, \quad (6.2)$$

$$(\phi_1 v_1 + \phi_2 v_2)_x = 0, \quad (6.3)$$

$$\mu_1 v_{1xx} - \phi_1 p_x + (v_2 - v_1) - \phi_{1x} (a(\theta)\phi_2 - b(\theta)\phi_1 - 2\chi(\theta)\phi_1\phi_2) = 0, \quad (6.4)$$

$$\mu_2 v_{2xx} - \phi_2 p_x + (v_1 - v_2) + \phi_{1x} (a(\theta)\phi_2 - b(\theta)\phi_1 - 2\chi(\theta)\phi_1\phi_2) = 0, \quad (6.5)$$

$$C_v \frac{\partial \theta}{\partial t} = (v_1 - v_2)^2 + \mu_1 (v_{1x})^2 + \mu_2 (v_{2x})^2 + \lambda \theta_{xx} \quad (6.6)$$

$$+ \theta \phi_{1x} (v_1 - v_2) (a_1 \phi_2 + b_1 \phi_1 - 2z_1 \phi_1 \phi_2) - c \theta_x (\phi_1 v_1 + \phi_2 v_2),$$

in  $\mathcal{R}_t$ ,

$$(v_f)_x = 0, \quad (6.7)$$

$$\mu_f v_{fxx} - p_{fx} = 0, \quad (6.8)$$

$$C_{fv} \frac{\partial \theta_f}{\partial t} = \mu_f (v_{fx})^2 - c_f \theta_{fx} v_f + \lambda_f \theta_{fxx}, \quad (6.9)$$

at  $x = L_\ell(t)$ ,

$$v_1 - v_f = (1 - \phi_1)(v_1 - v_2) = w, \quad (6.10)$$

$$\mu_f v_{fx} - \mu_2 v_{2x} - \mu_1 v_{1x} + [p] = 0, \quad (6.11)$$

$$(\varepsilon_f - \varepsilon_2 - [p])w + \frac{(\mu_2 v_{2x})}{\phi_2} w - \mu_f v_{fx} w + (\lambda_f \theta_{fx} - \lambda \theta_x) = 0, \quad (6.12)$$

$$\mu_\perp w = \mu_f v_{fx} - \frac{1}{\phi_2} \mu_2 v_{2x} + [p] + (\psi_2 - \psi_f), \quad (6.13)$$

at  $x = L_r(t)$ ,

$$v_f - v_1 = (1 - \phi_1)(v_2 - v_1) = w, \quad (6.14)$$

$$\mu_f v_{fx} - \mu_2 v_{2x} - \mu_1 v_{1x} + [p] = 0, \quad (6.15)$$

$$(\varepsilon_f - \varepsilon_2 - [p])w + \frac{(\mu_2 v_{2x})}{\phi_2} w - \mu_f v_{fx} w + (\lambda \theta_x - \lambda_f \theta_{fx}) = 0, \quad (6.16)$$

$$\mu_\perp w = \mu_f v_{fx} - \frac{1}{\phi_2} \mu_2 v_{2x} + [p] + (\psi_2 - \psi_f). \quad (6.17)$$

$$v_f = 0, \quad \theta_f = \frac{\theta_0}{\theta} \quad \text{at } x = 0, \quad (6.18)$$

$$v_f = 0, \quad \theta_f = \frac{\theta_1}{\theta} \quad \text{at } x = 1. \quad (6.19)$$

Through this model, we see that parameters which have effects on the system are  $\mu_1, \mu_2, \mu_\perp, a(\theta), b(\theta)$ , and  $\chi(\theta)$ . However, in real physical situations, mostly  $\mu_1, \mu_2 \approx 0$ , and we can set  $a(\theta) = 0, b(\theta) = 1$  for polymer solutions [29]. Moreover, we have no measurement of the parameter  $\mu_\perp$  which is firstly introduced in [23]. Accordingly, we investigate how the gel responds to various values of  $\chi(\theta)$  in the subsequent section.

## 6.2 Analytic Estimates and Simulations

First, we find conditions on the Flory-Huggins interaction parameter  $\chi(\theta)$  that allow two interfaces of the gel to move in the same direction simultaneously.

Consider a system in the following setting:

$$\begin{aligned} \mu_1 = \mu_2 = 0, \quad \mu_\perp = 1, \quad \kappa = 1, \quad k_B = 1, \\ C_v = C_{fv}, \quad \lambda_f = \lambda, \quad P_f = 0, \quad W_{\text{elas}}(\phi_1) = 0, \\ a(\theta) = 0, \quad b(\theta) = \theta, \quad \chi(\theta) = z_1\theta + z_0, \\ \theta_0 = 0, \quad \theta_1 = 1. \end{aligned} \quad (6.20)$$

Then by (5.16),(5.18) and (5.21),(5.23), interfaces each have their own velocity as a function of temperature and volume fraction of the polymer at the point:

$$\begin{aligned} v_1(L_\ell, t) &= (\psi_2 - \psi_f)(\theta_\ell, \phi_{1\ell}), \\ v_1(L_r, t) &= -(\psi_2 - \psi_f)(\theta_r, \phi_{1r}), \end{aligned}$$

where subindexes  $\ell$  and  $r$  respectively represent the left and right boundaries of the gel.

The difference of free energies of fluid inside and outside on the interface is of the form

$$\psi_2 - \psi_f = k_B \{ b(\theta) (\phi_1 + \ln(1 - \phi_1)) + \phi_1^2 \chi(\theta) \} = \theta (\phi_1 + \ln(1 - \phi_1)) + \phi_1^2 \chi(\theta).$$

Using the Taylor series expansion of the logarithm,  $\ln(1-\phi_1) = -\phi_1 - \phi_1^2/2 - \phi_1^3/3 - \dots$ , it is approximated up to the second order in  $\phi$  by

$$\phi_1^2 \left( -\frac{\theta}{2} + \chi(\theta) \right). \quad (6.21)$$

Thus both boundaries of the gel move in one direction, specifically in the positive direction, when the following inequalities are satisfied.

$$\phi_{1\ell}^2 \left( -\frac{\theta_\ell}{2} + \chi(\theta_\ell) \right) > 0, \quad \phi_{1r}^2 \left( -\frac{\theta_r}{2} + \chi(\theta_r) \right) < 0.$$

Substituting (6.20) into the above, we have

$$\left( z_1 - \frac{1}{2} \right) \theta_\ell + z_0 > 0, \quad \left( z_1 - \frac{1}{2} \right) \theta_r + z_0 < 0,$$

which deduces

$$z_1 < 1/2, \quad \left( \frac{1}{2} - z_1 \right) \theta_\ell < z_0 < \left( \frac{1}{2} - z_1 \right) \theta_r. \quad (6.22)$$

We note that if  $z_1 > 1/2$ , we have

$$\theta_\ell > \frac{-z_0}{z_1 - 1/2} > \theta_r,$$

which is impossible since  $\theta_\ell \leq \theta_r$  always. The case where  $z_1 = 1/2$  also provides unreasonable result as well.

Application of the preceding argument to the case when the interfaces move in the negative direction leads to

$$z_1 > 1/2, \quad -\left( z_1 - \frac{1}{2} \right) \theta_r < z_0 < -\left( z_1 - \frac{1}{2} \right) \theta_\ell. \quad (6.23)$$

From (6.21) in company with the bounds of  $z_0$  and  $z_1$ , (6.22) and (6.23), we expect that the boundaries of the gel should move faster as the magnitude of  $|z_1 - \frac{1}{2}|$  increases.

Next, we conduct simulations based on the algorithm given in Section 5.3 with physically realistic values for shear viscosities of polymer networks and fluid in the gel:

$$\mu_1 = \mu_2 = 0.01,$$



and initial conditions

$$\begin{aligned}\phi_1 &= 0.5 && \text{for } x \in [L_\ell(0), L_r(0)], \\ \theta &= \theta_f = 0.5 && \text{for } x \in [0, 1].\end{aligned}$$

Figures 6.2 and 6.2 show the evolution of the positions of gel boundaries with various Flory-Huggins parameter  $\chi(\theta)$  values in the cases of moving toward the right and the left, respectively.

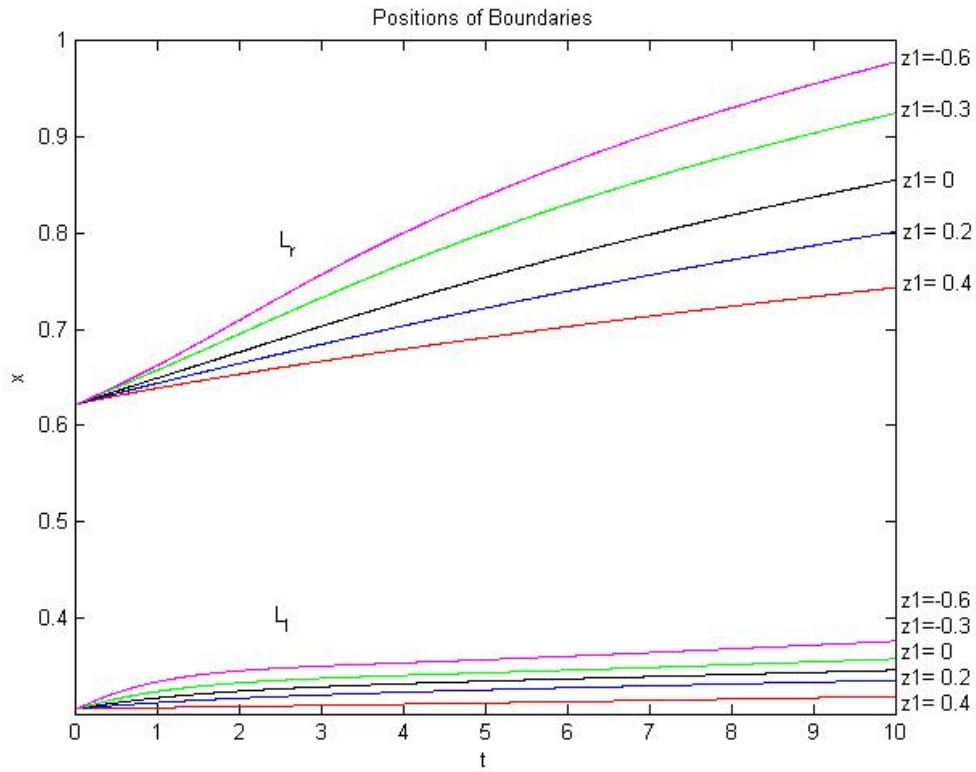


Figure 6.1: **(Positions of Two Moving Interfaces,  $L_\ell$  and  $L_r$ , to the Right)** The upper and lower curves represent the trajectories of the right and left interfaces of the gel, respectively. Each pair of trajectories is correspondingly plotted for  $\chi(\theta) = -0.6\theta + 0.65, -0.3\theta + 0.47, 0.32, 0.2\theta + 0.22, 0.4\theta + 0.12$ , where  $z_0$  values were chosen to implement the range in (6.22).

These numerical simulation results are coincident with the observation that smaller

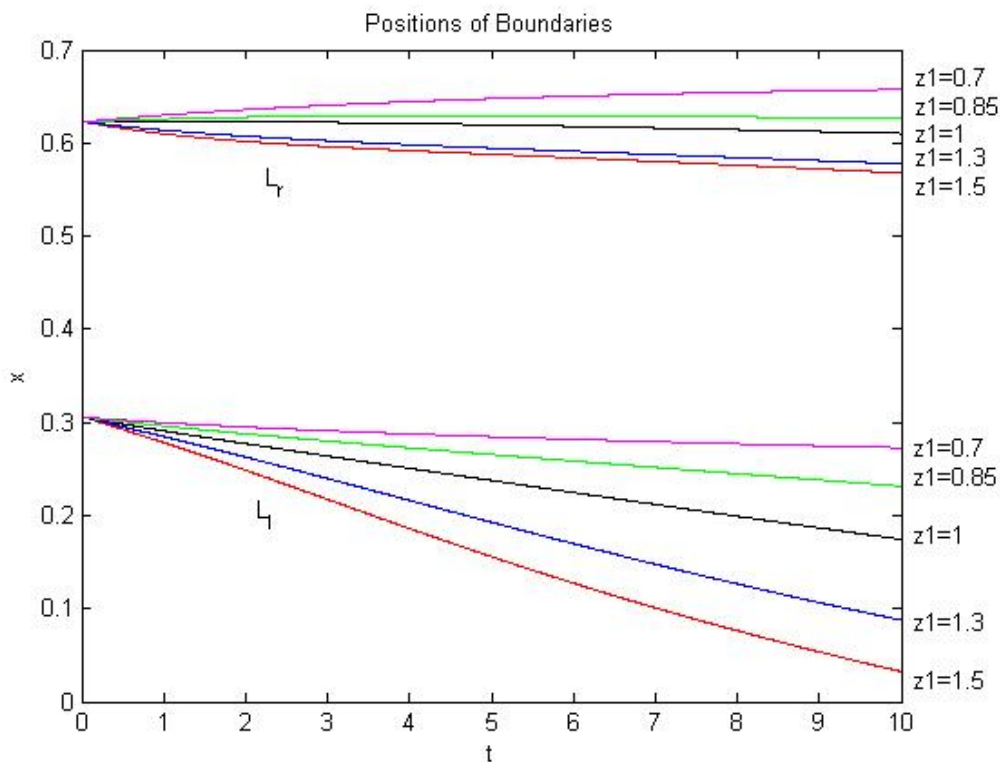


Figure 6.2: **(Positions of Two Moving Interfaces to the Left)** The upper and lower curves respectively are for the right and left interfaces of the gel, as in Figure 6.2. The paths are in correspondance with  $\chi(\theta) = 0.7\theta - 0.02, 0.85\theta - 0.09, \theta - 0.17, 1.3\theta - 0.3,$  and  $1.5\theta - 0.4$ .

difference between  $z_1$  and  $\frac{1}{2}$  makes the gel slow. What's more, the pictures demonstrate that the gap between velocities of two layers grows as  $z_1$  becomes farther from  $\frac{1}{2}$ . Specifically, the right(left) interface moves much faster than the left(right) one after very early stage when the gel moves in the positive(negative) direction. This means that the gel swells during the motion.

We interpret these phenomena in connection with osmotic pressure. Osmotic pressure is a measurement of the difference of free energies between a polymer solvent and a pure solvent. The osmotic pressure is calculated by differentiating the total free energy of mixing with respect to the volume of the polymer networks. We denote the osmotic

pressure by  $\Pi$  and it has the form

$$\begin{aligned}\Pi &\cong Ak_B\phi^2 \left( \frac{\theta}{2} - \chi(\theta) \right) \\ &= Ak_B\phi^2 \left( \left( \frac{1}{2} - z_1 \right) \theta - z_0 \right),\end{aligned}$$

where  $A$  is a positive constant. By (6.22), it is easily seen that the pressure is approximately proportional to  $\left(\frac{1}{2} - z_1\right)$ , and thus if  $z_1$  is lower and lower than  $\frac{1}{2}$ , the osmotic pressure is increased, which makes fluid better flow into the gel across the interface. Furthermore, different temperature values at both boundaries provide slightly different osmotic pressures, and hence allows passage of fluid through the gel, which is the driving force for moving interfaces. The case of moving gel to the left is understood in the same vein. Finally, we remark that as pictured in Figure 6.2, for the values of  $z_1$  between  $\frac{1}{2}$  and 1,  $L_r$  is slowly toward the right with higher temperature. This implies that temperature becomes a more decisive factor when  $\frac{1}{2} < z_1 < 1$ .

## Chapter 7

# Conclusion

In this thesis, we have developed and analyzed a model of polymer gels driven by thermal effects, and have performed numerical simulations of this model in a one-dimensional geometry to investigate several phenomena such as the evolution of the interface between the gel and the surrounding fluid.

The main contribution of my dissertation is the incorporation of thermal effects into the equations of gel dynamics. Including thermal effects has been a challenging problem. For soft matter systems, model equations are derived from Onsager's variational principle. This variational principle gives a framework for derivation of kinetic and evolution equations in irreversible process [22]. It works well in the case when temperature is kept constant and it leads to a system of force balance equations that result in free energy dissipation [24]. However, when change in temperature is involved, it becomes difficult to use this method. This analysis has been carried out only in very simple systems. When thermal effects are present, not only mass conservation and force balance but also energy balance is required, and thus, we must introduce an energy conservation law and derive equations so that entropy increases. Constructing an energy conservation law in gels is challenging because we treat gels as a two-phase medium. It turns out that an energy conservation law is required for each component. However, energy of gel is given as a whole in most cases. This difficulty is resolved by requiring that the energy function be "extensive", which leads to a natural splitting of the energy. From this, we have derived a system of equations that respects mass conservation, force balance(Chapter 3) and energy balances, and Galilean invariance, while satisfying an

entropy inequality(Chapter 4).

In developing a numerical method for the spatially one-dimensional model, Lagrangian coordinate system is adopted in order to avoid moving boundaries problem(Chapter 5). Finally, we have verified analytically and numerically that gels under an imposed thermal gradient can generate flow. In particular, in a one-dimensional model with Dirichlet boundary conditions, different temperature values at both sides make the osmotic pressures slightly different, which allows water to flow through the gel(Chapter 6).

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