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# Modelling Hydrogels with Onsager's Variational Principle

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# Abstract

The goal of this Master's thesis is to provide a physical and mathematical model that attempts to describe the deformation process of hydrogels. Hydrogels are commonly defined as three dimensional networks of hydrophilic polymers with the ability to retain a large quantity of water. When water enters, the network is capable of large and recoverable deformations similar to natural tissues. Moreover, some hydrogels change their degree of swelling in response to external stimuli. This, along with other unique properties, makes them a very interesting subject of research. In fact, they already have many applications in several scientific disciplines and in the industry. Describing the deformation process of hydrogels can be challenging for three reasons. Firstly, there is mass transport. Secondly, large deformations are possible, hence linear elasticity may not be applied. Lastly, since external physical stimuli such as heat or light may induce the deformations, a successful model needs to incorporate these stimuli as physical variables. In this thesis, I expose a variational model that is obtained with the Onsager's principle in an attempt to tackle these issues. In the first chapter, I provide an introduction to hydrogels along with their properties and applications. In the second chapter, I develop the main physical modelling assumptions that are needed to model hydrogels. In the third chapter, I expose a model proposed in [7], that uses the second principle of thermodynamics. In the fourth chapter, I provide an abstract formulation of the Onsager's principle, which I later use to derive the well known diffusion equation. In the fifth and last chapter, the Onsager's principle is applied and the constitutive equations for the motion of hydrogels are obtained which are very similar to the ones derived in [7]. In this case, though, the solution arises as the minimum of a functional. This provides an ideal setting for discretization and numerical analysis.

**Keywords:** Hydrogels, large deformations, mass transport, Onsager's variational principle, responsive gels

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# Chapter 1

## Introduction to Hydrogels

In this chapter, I provide an introduction to hydrogels. First, I describe their physical structure and their classification. Then, I list the most important types of responsive hydrogels and some of their applications. Most of the chapter is based on [3], [8], [9] [10], and [4].

### 1.1 Introduction

The three classic phases of matter on Earth are solid, liquid and gas. Change in pressure or temperature may cause a material to change from one phase to another. These categories cannot fully describe the full range of materials that are found in nature. Hydrogels provide an example of such materials.

Hydrogels are defined as cross-linked hydrophylic polymeric networks with the ability to swell and retain a large amount of solvent (usually water, or an ionic solution). As the solvent migrates inside and outside, the network swells and contracts. Often, the mass of the solvent is several (even hundreds) of times the mass of the network, because hydrogels are capable of large and recoverable deformations.

The ability of hydrogels to absorb water arises from hydrophilic functional groups attached to the polymers. The cross-links between the polymers prevent them from dissolving in the solvent and provide mechanical stability. Also, as solvent enters in the network, its entropy decreases because the polymers are stretched; on the other hand, the mixing entropy increases because the solvent diffuses through the network. Another key energetic fact is that, as the solvent flows through the network, energy is dissipated because of the viscous friction between the solvent molecules and the network. Because of this physical structure, hydrogels share properties with both solids and liquids. In fact, similarly to solids, hydrogels do not flow, and similarly to liquids, small molecules diffuse.

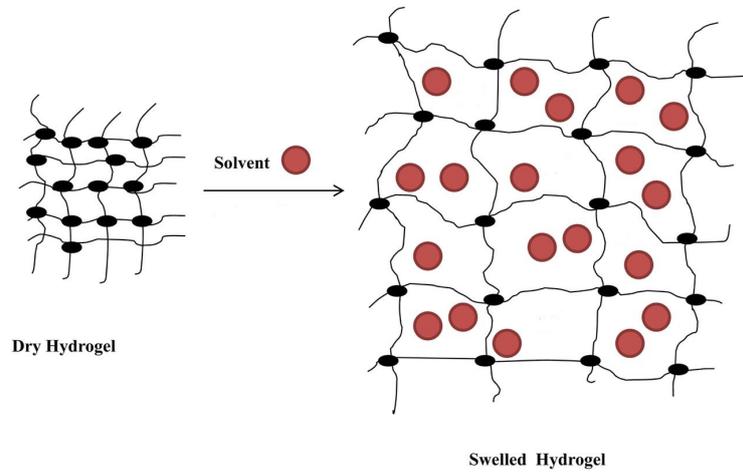


Figure 1.1: A polymeric network is shown schematically, before and after that a solvent is mixed inside of it. [11].

Several properties render hydrogels unique materials that can be suitable for many applications. Some of these include being biocompatible, being capable of large deformations with a degree of flexibility similar to natural tissues, being responsive to external stimuli, being biodegradable or bioabsorbable, and having good transport properties.

Both in Nature and in the industry there are several important examples of materials that fall into the category of hydrogels. For instance, acrylamide and potassium acrylate are used in agriculture to provide plants with a natural reservoir of water and nutrients during dry seasons. Two other examples are hydrogel contact lenses and wound healing hydrogel sheets.

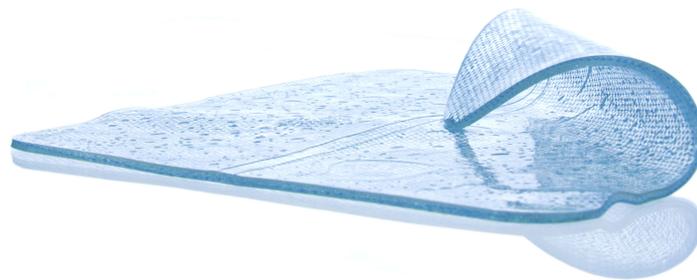


Figure 1.2: A hydrogel sheet. It is used to reduce local pain in superficial wounds and absorbs moisture from low exudating wounds.

## 1.2 Classification

Hydrogels can be divided into groups according to several criteria. The most important ones are listed below, each with a detailed description of the possible cases.

**Origin of the polymers:** The polymers that form a hydrogel can be either natural or synthetic.

Natural polymers are usually proteins such as collagen or polysaccharides such as chitosan. Hydrogels made of such polymers are both biocompatible and biodegradable, and they can even support cellular activities. On the other hand, they may carry pathogens or evoke an immune response. Moreover, they have low mechanical stability.

Synthetic polymers are made from monomers such as vinyl acetate, acrylamide and lactic acid. The synthesis of polymers can be changed in order to obtain hydrogels with specific properties. Also, synthetic hydrogels have a low risk of biological pathogens or of evoking an immune response. On the other hand, they are less prone to support biological activities and they may be not biodegradable or even toxic.

**Composition of the polymers:** The properties of hydrogels change also in function of the method with which they are formed.

When the polymer network is derived from a single species of monomers the hydrogel is said to be homopolymeric. On the contrary, copolymeric hydrogels are formed from two or more different monomer species that are arranged in a random or alternating configuration along the chain of the polymer network.

Multipolymer Interpenetrating polymeric hydrogels (IPN) are made of two groups of polymers that form two independent networks. In semi-IPN hydrogels, one group forms a polymer network, while the other group is not cross-linked, and dissolves in the solvent.

**Structure of the network:** Classification may also be based on the physical structure of the polymer chain: amorphous (random, non-crystalline), semi-crystalline (regions of partially ordered structure) or crystalline (network with an ordered structure).

**Electric charge:** Hydrogels may also have electric charges located on the polymers. Therefore, hydrogels can be nonionic (neutral), anionic or cationic.

**Type of cross-links:** As previously explained, hydrogels have cross-links between the polymers, which prevent the hydrogel from dissolving. These crosslinks can be of three types: physical, chemical or biochemical.

Physical hydrogels are usually formed from a liquid solution with change in temperature, ionic concentration, pH, or other conditions. Their polymer chains are connected by electrostatic forces, hydrogen bonds, hydrophobic interactions, or chain entanglements. Also, the crosslinks are usually weaker and easier to disrupt.

The polymer chains of chemical hydrogels are held together by permanent covalent bonds. Therefore, these hydrogels have higher mechanical stability and resistance to degradation. In biochemical hydrogels, biological agents like enzymes or amino acids take part in cross-links formations.

**Responsivity to external stimuli:** Some hydrogels are capable of dramatic structural changes when a certain stimulus is applied. For this reason, they are also called "smart" hydrogels. Therefore, a way to classify hydrogels is to consider whether they are responsive to external stimuli and, if they are, which stimuli these are.

The next section will explore in more detail some types of responsive hydrogels, and some of their applications. In fact, responsive hydrogels are currently the subject of intense research, especially for their promising applications in biomedical science, biotechnology, and pharmaceutical science.

### 1.3 Responsive hydrogels

Responsive hydrogels can be designed so that they swell or shrink when specific external conditions change. When certain physical or chemical stimuli are applied, the volume and the shape of this class of hydrogels change, even dramatically. Physical stimuli include temperature, electric or magnetic fields, light, pressure, and sound. Chemical stimuli include pH, solvent composition, ionic strength, and molecular species.

In most cases, the induced volume changes are reversible, which means that hydrogels are capable of returning to their initial state as soon as the stimulus is removed. The magnitude of the reaction is determined by the nature of the polymers, the charge density, the types of crosslinks and the intensity of the external stimulus. In the remaining part of the chapter, I describe some types of responsive hydrogels along with few applications.

**Temperature responsive hydrogels:** These hydrogels originate from polymeric solutions that became gel after a change in temperature. Temperature responsive hydrogels have hydrophobic groups such as methyl, ethyl, and propyl, that interact with water molecules by hydrogen bonds. Most of these hydrogels increase their solubility as temperature increases. In some cases, solubility decreases with an increase in temperature.

In general, there is a critical temperature, called the lower critical solution temperature (LCST), that works as a transition point. For example, positive thermosensitive hydrogels swell below the LCST and collapse for higher temperatures. This makes these hydrogels particularly suitable for controlled drug delivery.

**pH responsive hydrogels:** This class of hydrogels contain acidic or basic groups that respond to local pH changes by gain or loss of protons. Polyelectrolytes are polymers with a large number of such ionizable groups.

Anionic polyelectrolytes such as poly(acrylic acid) (PAA) are deprotonated in basic environmental conditions. Then, electrostatic repulsions between the chains strongly increase, causing the network to stretch. Thus, water molecules enter into the network, and its volume grows. However, in an acidic media, the acidic polymer gains protons. This results in less charge density, making the network collapse. In contrast, cationic polyelectrolytes swell in acidic media and collapse in basic media. There is also a third kind of reaction: amphiphilic hydrogels contain both acidic and basic groups. Therefore, they exhibit two-phase transitions in both acidic and basic environments. In the following figure there is a visual comparison between the three different types.

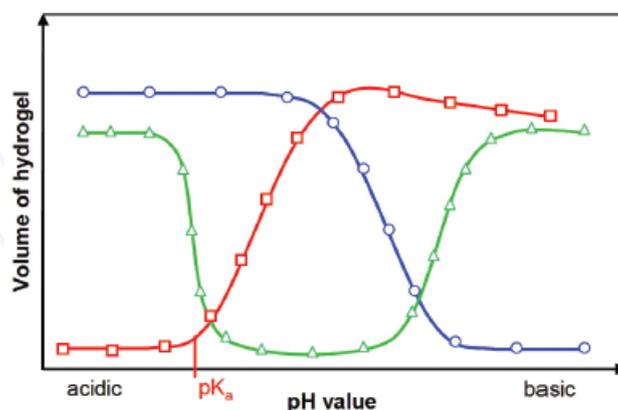


Figure 1.3: Behavior of polyelectrolyte hydrogels: acidic hydrogels (curve with squares), basic hydrogels (curve with circles), and amphiphilic hydrogels (curve with triangles) which show two-phase transitions. [3]

**Photo responsive hydrogels:** This class of hydrogels is affected by light of the appropriate wavelength. Also in this case, the change is triggered by specific functional groups that are attached to the polymers. An example of such groups is chromophores. Chromophores act by absorbing the light from a specific wavelength and then dissipating it locally as heat. This increase the temperature (locally) which in turn alters the swelling behavior.

**Electro responsive hydrogels:** These hydrogels, as the pH responsive ones, are usually composed of polyelectrolytes. In the presence of an electric field, the charges are subjected to the electrical force. So, mobile ions are attracted to the electrodes. As a result, the hydrogel can swell and shrink regionally at the cathode and anode. The difference in ion concentration in the network, in turn, leads to the hydrogel bending.

During this process, electrical energy is transformed into mechanical energy, hence these hydrogels have promising applications in biomechanics, sensing, sound dampening, chemical separations, controlled drug delivery, and tissue engineering. For example, hydrogels of acrylamide and carboxylic acid derivatives, like PAA, have been utilized as electro sensitive and bio-compatible smart muscle based devices.

## 1.4 Applications

As explained before, hydrogels have several applications. Here I will explain here a few of these applications. Moreover, I will provide some explanations regarding the possible structural changes that can be made on hydrogels so that they perform better the designed task.

**Dyes and heavy metal ions removal:** Many industrial processes result in the production of heavy metal pollution that leads to severe threats to public health and ecological systems. Therefore, removing heavy metal ions from water resources is a very important task; but, it is also very difficult to accomplish. Some currently used techniques include filtration, chemical precipitation, ion-exchange, and adsorption. Adsorption is an attractive method because it is efficient, easy to operate, low cost and different adsorbents are available.

Hydrogels have been used for removing heavy metal ions from waste water due to their high adsorption capacities. Additionally, their regenerative abilities make it possible to reuse them, and the ability of joining different functional groups to the network makes them versatile for the treatment of many types of waste. The modification of these functional groups can also result in a greater speed of adsorption and a higher adsorption capacity.

However, hydrogels often have some limitations, such as low mechanical stability. A possible solution is to add various clay minerals in the hydrogel matrix in order to improve mechanical stability and swelling ability. Another proposed technique to improve efficiency is to use laponite as multifunctional cross-links. The following figure, shows a hydrogel before and after adsorption of pollutant molecules.

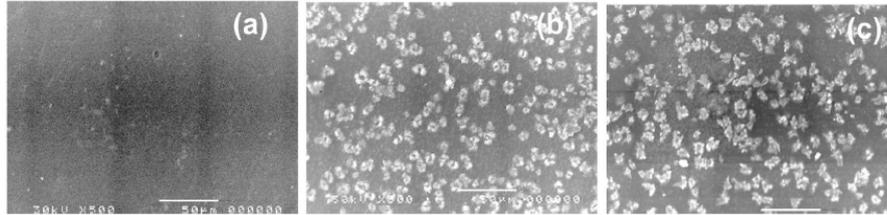


Figure 1.4: Surface of dimethyl amino ethyl methacrylate and acrylic acid (DMAEMA/AAc) with a weight ratio of 80/20. (a) Before metal uptake; (b) After adsorption of  $Cu^{+2}$ ; and (c)  $Co^{+2}$  metal ions with solution concentration 1000 ppm and pH 5 after 24 hours. [10].

**Drug delivery:** Controlled drug delivery systems (DDS), which are used to deliver drugs at certain rates for predefined periods of time, have been used to overcome the limitations of regular drug formulations. Hydrogels are particularly suitable for this because they are hydrophilic, biocompatible, and their drug release rates can be controlled by local changes in pH, temperature, or other external stimuli. For instance, the human body exhibits variations in pH along the gastrointestinal tract as well as in some specific areas such as certain tissues.

In general, the delivery rate of the drug can be adjusted by controlling the degree of swelling, crosslinks density, and degradation rate. As a matter of fact, the possibility of releasing pharmaceuticals for long periods of time (sustained release) is the main advantage obtained from hydrogels. Moreover, hydrogels are highly permeable to different kinds of drugs, making them very versatile.

## Chapter 2

# The Foundations of Hydrogels Modelling

### 2.1 Introduction

As previously discussed, hydrogels are a very particular class of materials. In fact, their state is neither liquid nor solid. They are formed by the interaction of a three-dimensional network of hydrophilic polymers, and a solvent, whose molecules flow inside and outside of it. Inside of the network, the solvent is able to flow freely just like a fluid. So, as solvent molecules enter or exit the network, hydrogels are capable of large and recoverable deformations. Moreover, the polymers do not dissolve into the solvent because of their length and the presence of cross-links between them.

From these key features, it follows that a successful modelling framework must couple large deformations with mass transport. Therefore, linear elasticity may not be applied. In this chapter, the main physical properties and formulas are presented. These are the starting points for developing a model that successfully describes mass transport and large deformations.

### 2.2 The motion of the solvent

As explained in [7], when solvent molecules flow inside (or outside) of the network, the dimension and shape of the hydrogel change in the two following ways.

- **Local rearrangement.** Local rearrangement is when, inside of the hydrogel, solvent molecules move locally without crossing the polymer chain of the network. This affects the shape of the hydrogel, but not its volume. This process is very rapid and its time scale does not depend on the hydrogel's volume. Also, there is no substantial dissipation of energy.

- **Long range migration.** In this case, the solvent molecules cross one or more layers of polymers. This takes into account both when solvent molecules enter (or exit) the network, and when solvent molecules change their position inside of the network enough that at least one layer of polymers is crossed. So, not only the shape of the network, but also its volume may be affected. This process is slower and its time scale is proportional to the total volume. Also, since polymers crossing is involved, energy is dissipated.

As explained above, during long range migration, energy is dissipated. So, even though the polymers have recoverable deformations, the process itself is irreversible in the sense that the entropy is always increasing. This is caused by the viscous friction generated when the velocity of the solvent molecules is different from the velocity of the network and, consequently, the molecules cross one or more layers of polymers. Following the work of [7], local arrangement will be regarded as instantaneous, and it does not dissipate energy.

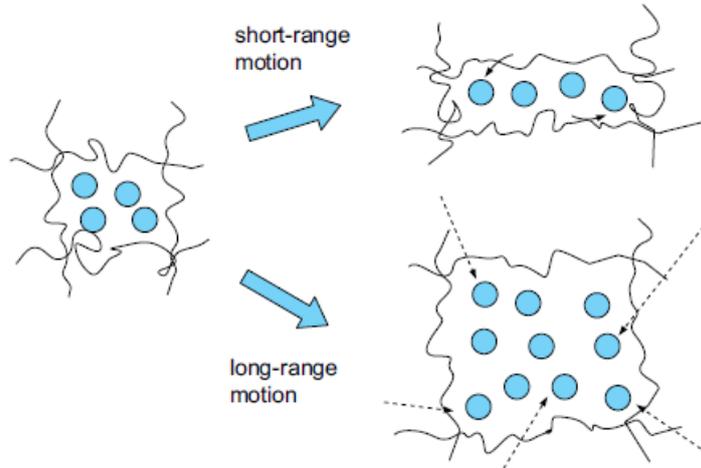


Figure 2.1: A representation of the two types of solvent motion. [7].

In general, the motion of the solvent, and the resulting deformation of the network, are driven by two physical principles that work against each other. If, for example, solvent molecules are entering into the network, then:

1. The configurational entropy of the network decreases because the polymers are stretched, and network grows in volume.
2. The mixing entropy between the polymers, and the solvent increases as the latter diffuses inside of the network.

## 2.3 The modelling assumptions

At time  $t = 0$ , a dry polymer occupies the region  $\Omega_0 \subset \mathbb{R}^3$ . This is the reference configuration that we choose for the physical motion. At every other time  $t$ , a solvent is mixed *everywhere* inside of the network. The resulting mixture is a hydrogel that at time  $t$  occupies the region  $\Omega$ . Its motion over time is mapped by  $x = \phi(X, t)$ .

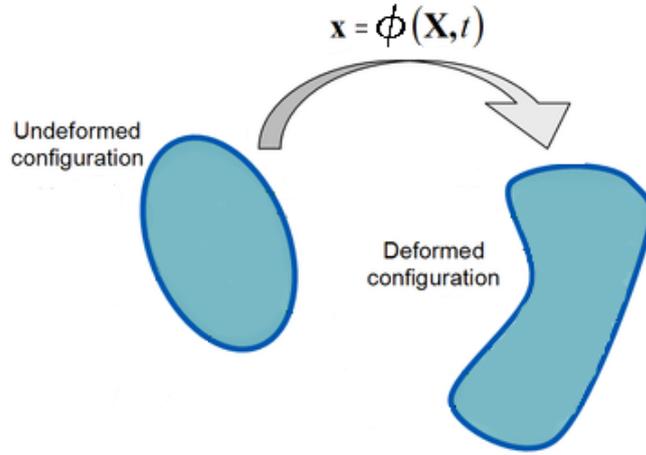


Figure 2.2: A schematic representation of the deformation map.

The following notation and properties from continuum mechanics will be used (a complete explanation can be found in [1]).

- $F := \partial\phi(X, t)/\partial X$  is the deformation gradient, and  $J = \det(F)$ . Also,

$$\partial_t J(X, t) = JF^{-\top} : \nabla_0(V). \quad (2.1)$$

- If  $dV$  is an infinitesimal volume in the reference configuration  $\Omega_0$ , then its deformed image  $dv$ , under  $\phi$ , is

$$dv = JdV. \quad (2.2)$$

If  $dS$  is an infinitesimal surface element in  $\Omega_0$  with normal vector  $N$ , and  $ds$  is its deformed image with normal vector  $n$ , then

$$nds = JNF^{-\top}dS. \quad (2.3)$$

- $\sigma$  is the Cauchy stress tensor and  $P = J\sigma F^{-\top}$  is the first Piola tensor.

- The Lagrangian gradient and divergence of the field  $U(X, t)$  are written respectively as  $\nabla_0 U$  and as  $\nabla_0 \cdot U$ . The eulerian gradient and divergence of  $U(x, t)$  are  $\nabla U$  and  $\nabla \cdot U$ . Moreover, we have the important formulas

$$\nabla \cdot U = F^{-\top} : \nabla_0 U. \quad (2.4)$$

Above, there is an abuse of notation. In fact, the correct expressions of the eulerian gradients and divergence are  $\nabla U = \nabla(U \circ \phi^{-1})$  and  $\nabla \cdot U = \nabla \cdot (U \circ \phi^{-1})$ . From now on, when an equation has both variables written in Lagrangian coordinates and variables written in eulerian coordinates, there is always assumed to be the composition with  $\phi$  or  $\phi^{-1}$ .

- In general, for any scalar field  $f$ , vector field  $v$  and tensor  $A$

$$\nabla \cdot (v^\top A) = \nabla(v) : A + v^\top \nabla \cdot (A) \quad (2.5)$$

$$\nabla \cdot (fv) = \nabla(f)^\top v + f \nabla \cdot (v). \quad (2.6)$$

Also, recall that for any  $\Omega$  with  $\partial\Omega$  regular enough

$$\int_{\Omega} \nabla \cdot v \, dV = \int_{\partial\Omega} v^\top n \, dS, \quad (2.7)$$

where  $n$  is the normal vector to  $\partial\Omega$ .

In order to model the deformation of the hydrogel and the diffusion of the solvent through the network, we make the four following assumptions from which all the results will be derived.

- The network is incompressible and elastic.
- The solvent is taken into account by assigning a molecular density  $c$  to every point  $x \in \Omega$ . Moreover, inertial forces can be neglected because hydrogels operate in very slow regimes, or at very small scales.
- The newly introduced density  $c$  is able to flow with a velocity  $v^f(x, t)$  that, in general, is different from the velocity of the network  $v(x, t)$ .
- The volume of  $\Omega$  grows as the solvent mixes with the network. Therefore, it is the sum of the volume of the network and the volume of the solvent.

Each of the above assumptions have specific physical consequences. In the next paragraph, the consequences of each assumption are analyzed in detail. Also, we will regard  $X$  as points belonging to the undeformed network and  $x = \phi(X, t)$  as their position during the motion at time  $t$ .

**Consequence of (a):** Since the network is elastic, there exists a function  $\Psi^N(F)$  such that  $\partial\Psi(F)/\partial F = P$ , and such that the free energy due to the network being deformed is

$$E^N = \int_{\Omega_0} \Psi(F) dV. \quad (2.8)$$

**Consequence of (b):** The molecular density (number of solvent molecules per unit volume) in eulerian coordinates is the function  $c(x, t)$  such that for every  $A \subset \Omega$ , at time  $t$ , the number  $N(A, t)$  of solvent molecules inside  $A$  is

$$N(A, t) = \int_A c(x, t) dv. \quad (2.9)$$

If  $A_0 = \phi^{-1}(A, t)$  is the undeformed volume, then, using equation 2.2,

$$N(A, t) = \int_A c(x, t) dv = \int_{A_0} c(\phi(X, t), t) J dV. \quad (2.10)$$

The Lagrangian counterpart of  $c$ , is the function  $C(X, t)$  such that, for every subset  $A \subset \Omega$ , at time  $t$ , we have

$$N(A, t) = \int_{A_0} C(X, t) dV \quad \text{with} \quad A_0 = \phi^{-1}(A, t). \quad (2.11)$$

The difference between  $c$  and  $C$  is that the first is calculated with respect to infinitesimal eulerian volumes  $dv$ , and the second with respect to infinitesimal Lagrangian volumes  $dV$ . In formulas,

$$c(x, t) = \lim_{dv \rightarrow 0} \frac{N(dv, t)}{dv} \quad \text{and} \quad C(X, t) = \lim_{dV \rightarrow 0} \frac{N(dV, t)}{dV}, \quad (2.12)$$

where  $dV = \phi^{-1}(dv, t)$ . Also, with the above notation, it is obvious that  $N(A, t) = N(A_0, t)$  for any  $A$  and  $A_0$  such that  $A_0 = \phi^{-1}(A, t)$ .

Finally, using equations 2.10 and 2.11, it is possible to see that  $c$  and  $C$  have the following relationship

$$C(X, t) = c(x, t) J(X, t) \quad \text{with} \quad x = \phi(X, t). \quad (2.13)$$

**Consequence of (c):** Given that the solvent velocity is  $v^f$ , the conservation of mass for the solvent gives the important formula

$$\partial_t c = -\nabla \cdot (c v^f). \quad (2.14)$$

Later, we will generalize this problem by saying that there is a pumping function  $r(x, t)$  which is defined as the number of solvent molecules injected in  $x$  per unit time and per unit deformed volume  $dv$ .

In this case, the principle of conservation of mass becomes

$$\partial_t c = -\nabla \cdot (cv^f) + r. \quad (2.15)$$

It is important to notice that  $r$ , just like  $c$ , is defined as a molecular density calculated with respect to the limit of infinitesimal eulerian volumes  $dv$ . Its Lagrangian counterpart  $r_0(X, t)$ , which is the number of solvent molecules injected per unit time per unit reference volume, satisfies

$$r_0(X, t) = r(\phi(X, t), t)J(X, t). \quad (2.16)$$

This follows from the same reasoning that yielded 2.13.

**Consequence of (d):** Take an infinitesimal volume  $dV$  around  $X$ . Then, at time  $t$ , the volume of its infinitesimal image  $dv$  (which is around  $x$ ) is equal to  $dV$  plus the volume of the solvent mixed. So, if  $C(X, t)$  is the molecular density at  $X$ , and  $k$  is the volume of a single solvent molecule,

$$dv = dV + kCdV = (1 + kC)dV.$$

Therefore, using that  $dv = JdV$ , we get

$$1 + kC(X, t) = J(X, t), \quad (2.17)$$

which is the so called molecular incompressibility constraint.

Differentiating 2.17 yields

$$k\partial_t C - JF^{-\top} : \nabla_0(V) = 0. \quad (2.18)$$

This formula will be very useful later, because it is the rate form of the molecular incompressibility constraint. In order to apply the Onsager's principle the rate form will be needed.

To summarize, we have obtained the following important formulas;

- $1 + kC = J$  the molecular-incompressibility constraint, and its rate version that is  $k\partial_t C - JF^{-\top} : \nabla_0(V) = 0$ .
- The relationship between  $c$  and  $C$ , which is  $C = Jc$ .
- The conservation of mass for the solvent  $\partial_t c = -\nabla \cdot (cv^f) + r$ .

## Chapter 3

# Standard Formulation for the Mechanics of Hydrogels

### 3.1 Introduction

In this chapter, I expose the theory developed in [7]. In this paper, the authors provide a model for the motion of hydrogels based on the second law of thermodynamics.

Initially, the governing equations are obtained by means of balance principles. Subsequently, the free energy  $G$  of the system is written in terms of the relevant physical quantities. Some quantities include the molecular density  $C$ , the deformation map  $\phi$ , the flux of the solvent  $\tilde{J}$ , and a newly introduced variable  $\mu$  which is the chemical potential. Then, by the second law of thermodynamics, it is imposed that  $\partial G/\partial t \leq 0$ . This leads to the constitutive equations.

### 3.2 The model

As discussed in the previous chapter, the main idea of the model is that as the function  $\phi$  maps the motion of the network over time, the solvent is taken into account by assigning a molecular density  $C$  to each point of the network. It is important to note, though, that this formulation does not explicitly use the fact that the solvent has a velocity  $v^f$  which, in general, differs from the velocity  $v$  of the network. So, of the equations 2.13, 2.17 and 2.15, only the first two are used.

First of all, the balance of momentum, and the balance of mass for the solvent yields the governing equations.

**Balance of momentum.** The forces acting on the system are

1.  $B(X, t)$  which is the body force acting on  $\Omega_0$ . For example, when one studies electro-responsive hydrogels, the electric field is a relevant body force  $B$ .
2.  $T(X, t)$  which is the surface tension on  $\partial\Omega_0$ .

Given the above quantities, another important assumption is made: inertial forces are negligible. This is due to the fact that the process is slow and it involves small scales. Hence, the inertial term does not appear in the First Cauchy equation which is

$$\begin{cases} \nabla_0 \cdot (P) + B = 0 & \text{in } \Omega_0 \\ P \cdot N = T & \text{in } \partial\Omega_0 \end{cases} \quad (3.1)$$

where  $N$  is the normal vector to  $\partial\Omega_0$ , and  $P$  is the first Piola tensor.

**Balance of mass for the solvent.** Consider the following functions:

1.  $r_0(X, t)$  is the number of solvent molecules injected per unit time, per unit volume, in  $\Omega_0$ . Physically it represents a pumping function acting on each point  $X \in \Omega_0$ .  
Admittedly, this might not make sense for 3D hydrogels since exchange of solvent happens only at the boundary. Nevertheless, it becomes important when one approximates hydrogels as 2D bodies. For example, if  $\Omega_0 \subset \{z = 0\}$  is a two-dimensional hydrogel, then  $r_0$  models the external contribution of the solvent that comes along the  $z$  direction.
2.  $i(X, t)$  is the number of solvent molecules injected per unit time, per unit area, in  $\partial\Omega_0$  (if the hydrogel is 2D,  $i$  is per unit length, and not per unit area).
3.  $\tilde{J}(X, t)$  is the flux vector of the solvent through  $\partial\Omega_0$ .

Then, since the number of molecules must be conserved, we have

$$\begin{cases} \partial_t C + \nabla_0 \cdot (\tilde{J}) = r_0 & \text{in } \Omega_0 \\ \tilde{J} \cdot N = -i & \text{in } \partial\Omega_0 \end{cases} \quad (3.2)$$

*Remark.* From an energetic point of view, we require that as the solvent flows inside of  $\Omega_0$  or across  $\partial\Omega_0$ , energy is dissipated. In particular, we define the chemical potential  $\mu$  such that the power due to the network-solvent mixing is

$$P = \int_{\partial\Omega_0} \mu r_0 dV + \int_{\partial\Omega_0} \mu i dS. \quad (3.3)$$

The chemical potential is defined as the energy required to add one molecule of solvent into the system. Physically, it means that as the solvent flows inside or outside of the network, the energy of the system changes. This causes the mixing entropy to change and to eventually balance out the configurational entropy of the network.

The total power is 3.3 plus the mechanical power. Therefore, it is

$$P(\phi, \mu, r_0, i) = \int_{\Omega_0} [B \cdot V + \mu r_0] dV + \int_{\partial\Omega_0} [T \cdot V + \mu i] dS. \quad (3.4)$$

The free energy of the system receives two distinct contributions.

- The energy due to the network stretching, with energy density  $W^N(F)$ .
- The energy of the solvent mixing, with energy density  $W^S(C)$ .

In other words,

$$E[\phi, C] = \int_{\Omega_0} [W^N(F) + W^S(C)] dV. \quad (3.5)$$

**Example 1.** As an example, for ideal gases the free energy due to mixing can be written as

$$W^S(C) = RTC(\log(C) - 1) + C\mu^*, \quad (3.6)$$

where  $T$  is the absolute temperature,  $R$  is the universal gas constant, and  $\mu^*$  is a normalization constant.

Now,  $P$  and  $E$  are given. From the second law of thermodynamics, if  $G = \partial_t E - P$ , then for every  $\phi, C, \mu, r_0$  and  $i$ , we must have

$$\partial_t G \leq 0. \quad (3.7)$$

*Remark.* This fundamental requirement is a way to impose mathematically that, over time, the system is dissipating energy (the entropy is increasing).

Moreover, the molecular incompressibility constraint can be included by defining a new  $K$  functional as

$$K = \partial_t G + \int_{\Omega_0} \left[ \Pi (k\partial_t C - JF^{-\top} : \nabla_0(V)) \right] dV \quad (3.8)$$

where  $\Pi$  is a Lagrangian field of multipliers.

*Remark.* We used  $k\partial_t C - JF^{-\top} : \nabla_0(V) = 0$  instead of  $1 + kC - J = 0$ , because, as previously discussed, it is the rate version of the latter and it contains the variables  $\partial_t C$  and  $V$ .

**Proposition 3.2.1.** *The condition  $K \leq 0$  is satisfied by the constitutive equations*

$$P = \frac{\partial W^N}{\partial F} - \Pi J F^{-\top} \quad (3.9)$$

$$\mu = k\Pi + \frac{\partial W^S}{\partial C} \quad (3.10)$$

$$\tilde{J} = -CM\nabla_0(\mu), \quad (3.11)$$

where  $M$  is symmetric and definite positive.

*Proof.*

$$\begin{aligned} K &= \int_{\Omega_0} \left[ \frac{\partial W^N}{\partial F} : \nabla_0(V) + \frac{\partial W^S}{\partial C} \partial_t C - V^\top B - \mu r_0 \right] dV - \int_{\partial\Omega_0} \left[ V^\top T + \mu i \right] dS \\ &\quad + \int_{\Omega_0} \left[ \Pi (k \partial_t C - \Pi J F^{-\top} : \nabla_0(V)) \right] dV \\ &= \int_{\Omega_0} \left[ \nabla_0(V) : \left( \frac{\partial W^N}{\partial F} - \Pi J F^{-\top} \right) - V^\top B \right] dV - \int_{\partial\Omega_0} V^\top T dS \\ &\quad + \int_{\Omega_0} \left[ \partial_t C \left( \frac{\partial W^S}{\partial C} + k\Pi \right) - \mu r_0 \right] dV - \int_{\partial\Omega_0} \mu i dS. \end{aligned}$$

Using 3.1 and 3.2, substitute  $B = -\nabla_0 \cdot (P)$  and  $r_0 = \partial_t C + \nabla_0 \cdot (\tilde{J})$  and get

$$\begin{aligned} K &= \int_{\Omega_0} \left[ \nabla_0(V) : \left( \frac{\partial W^N}{\partial F} - \Pi J F^{-\top} \right) + V^\top \nabla_0(P) \right] dV - \int_{\partial\Omega_0} V^\top T dS \\ &\quad + \int_{\Omega_0} \left[ \partial_t C \left( \frac{\partial W^S}{\partial C} + k\Pi - \mu \right) - \mu \nabla_0 \cdot (\tilde{J}) \right] dV - \int_{\partial\Omega_0} \mu i dS. \end{aligned}$$

Then, use 2.5 and 2.6, so

$$\begin{aligned} K &= \int_{\Omega_0} \left[ \nabla_0(V) : \left( \frac{\partial W^N}{\partial F} - \Pi J F^{-\top} - P \right) + \nabla_0 \cdot (V^\top P) \right] dV - \int_{\partial\Omega_0} V^\top T dS \\ &\quad + \int_{\Omega_0} \left[ \partial_t C \left( \frac{\partial W^S}{\partial C} + k\Pi - \mu \right) + \tilde{J}^\top \nabla_0(\mu) + \nabla_0 \cdot (\mu \tilde{J}) \right] dV - \int_{\partial\Omega_0} \mu i dS. \end{aligned}$$

Applying formula 2.7, and recalling  $PN = T$  and  $\tilde{J}^\top N = -i$ , finally yields

$$\begin{aligned} K &= \int_{\Omega_0} \left[ \nabla_0(V) : \left( \frac{\partial W^N}{\partial F} - P - J\Pi F^{-\top} \right) + \partial_t C \left( \frac{\partial W^S}{\partial C} + k\Pi - \mu \right) \right] dV \\ &\quad + \int_{\Omega_0} \left[ \nabla_0(\mu)^\top \tilde{J} \right] dV. \end{aligned}$$

From this, it is clear that the three previous equations satisfy  $K \leq 0$ .  $\square$

The equation 3.9 is simply incompressible hyperelasticity of the network. The equation 3.10 is Darcy's law and the equation 3.11 links the chemical potential with the mixing entropy. Also, physically, the multiplier  $\Pi$  represents the osmotic pressure.

In the next chapters, the underlying variational structure of this model is revealed with Onsager's principle. This variational approach will provide a functional whose minimal solution is the motion of the hydrogel. Moreover, it will provide a convenient setting for discretizing the system and performing numerical simulations.

## Chapter 4

# The Onsager's Variational Principle

In this chapter, I expose the Onsager's variational principle with the notation and the concepts of [6] and [5]. Moreover, I will use it to deduce the dissipation equation in order to provide a specific example before applying it, in the next chapter, for the study of hydrogels.

### 4.1 Introduction

The Onsager's variational principle has been recently used for describing dissipative systems in soft matter modelling. This principle holds for dissipative systems that satisfy certain conditions.

For example, following [2], consider a discrete set of particles moving in a fluid under a potential force  $U$ . Their position at time  $t$  is  $x = (x_1, \dots, x_n)$ . Also, these particles are experiencing a viscous friction as they flow in the fluid. Then, the equation of the motion satisfies

$$-D\dot{x} - \nabla(U(x)) = 0, \quad (4.1)$$

where  $D = d_{ij}$  is the matrix of the friction coefficients. If these coefficients are symmetric, which means  $d_{ij} = d_{ji}$ , then

$$x = \operatorname{argmin}_{\dot{x}} R(x; \dot{x}) \quad (4.2)$$

where  $R$  is the functional

$$R(x; \dot{x}) = \dot{U}(x) + \dot{x}^\top D \dot{x}. \quad (4.3)$$

The main idea is that the symmetry of the coefficients has let us find a dissipation potential  $\dot{x}^\top D \dot{x}$ . This is not possible for all physical processes. For instance, when there is a magnetic field or a Coriolis effect this idea may not be applied. Nevertheless, for the analysis of hydrodynamics problems this principle can be applied.

## 4.2 The Onsager's variational principle

There are many advantages associated with the use of the Onsager's principle, and each of them plays a fundamental role in modelling the mechanical behavior of hydrogels. This variational principle has the following properties.

- It describes the dynamics of dissipative systems. This is important because, as previously explained, energy is dissipated during the deformation process of hydrogels.
- It is applicable in fully nonlinear settings. This characteristic is particularly important for hydrogels (and more generally for biological tissues) modelling, because of the fact that they are capable of large, nonlinear deformations.
- It can be coupled with different physics. As seen in the first chapter, many types of external physical stimuli are important factors in the motion of responsive hydrogels.
- It provides a convenient setting for discretizing in space and time.

This variational principle has the following requirements.

1. The system is described by state variables  $X(t)$ , and there exist vector fields  $V$  such that for some operator  $Q$

$$\partial_t X = Q(X)V. \quad (4.4)$$

2. There are the free energy  $F(X)$ , and the power external supply  $P(X; V)$ .
3. There exists a dissipation potential  $D(X; V)$  that is convex in  $V$ , non-negative and such that  $D(X; 0) = 0$ .

*Remark.* Often,  $F$  is nonlinear. Also, even though  $P$  and  $D$  can be nonlinear in both arguments, often  $P$  is linear in  $V$  and  $D$  is quadratic in  $V$ .

Then, we define the *Rayleighian* as

$$R(X; V) = \dot{F}(X) + D(X; V) + P(X; V) \quad (4.5)$$

$$= DF(X)Q(X)V + D(X; V) + P(X; V). \quad (4.6)$$

The Onsager's principle states that the system evolves such that

$$V = \operatorname{argmin}_W R(X; W). \quad (4.7)$$

*Remark.* If the state variables  $X$  are subjected to a constraint  $\mathbb{C}(X)V = 0$ , it is possible to include it in the formulation by adding a field of Lagrangian multipliers  $\Lambda$ . Then, the functional to minimize is

$$L(X; V, \Lambda) = DF(X)Q(X)V + D(X; V) + P(X; V) + \Lambda\mathbb{C}(X, V). \quad (4.8)$$

### 4.3 An application

In order to understand how the principle works, I have used it to derive the diffusive equation as exposed in [5].

Consider a quiescent fluid occupying a region  $\Omega_0$  that is fixed over time. The molecules of a given substance are mixed in the fluid. Also, assume that the boundary  $\partial\Omega_0$  is impermeable. At time  $t$ , denote with  $C(X, t)$  the molar density.

The free energy of the system can be written using the ideal gas mixing entropy, so it becomes

$$E = RT \int_{\Omega_0} \left[ C(\log(C) - 1) + C\mu_0 \right] dV, \quad (4.9)$$

where  $\mu_0$  is a normalization constant. Then,

$$\partial_t E = RT \int_{\Omega_0} \left( \mu_0 + RT \log(C) \right) \partial_t C dV. \quad (4.10)$$

From the above equation, it appears that the quantity  $\mu(C) := \mu_0 + RT \log(C)$  measures the energy cost of mixing one mole of solute per unit volume in function of the current concentration  $C$ . It is called chemical potential. Also, it follows that  $\mu_0$  is the reference chemical potential for the reference configuration (in this case  $C = 1$ ).

Since the boundary is impermeable and there is no exchange with the outer environment, the power term  $P$  does not appear. Therefore, only the dissipation term is missing. The viscous force experienced by the solute molecules is  $F = -\nu N_A V_f$  where  $\nu$  is the drag coefficient,  $N_A$  is the Avogadro number and  $V_f$  is the velocity field of the solute particles. So, the dissipation potential can be written as,

$$D = \frac{\nu N_A}{2} \int_{\Omega_0} C |V_f|^2 dV. \quad (4.11)$$

The Rayleighian becomes,

$$R(C; V_f) = RT \int_{\Omega_0} \left[ \left( \mu_0 + RT \log(C) \right) \partial_t C + \frac{\nu N_A}{2} C |V_f|^2 \right] dV. \quad (4.12)$$

The Rayleighian term can not be minimized yet because of the term  $\partial_t C$ . A process operator is needed in order to write  $\partial_t C$  in function of  $V_f$ . In fact,  $R$  needs to be minimized with respect to  $V_f$ . This is possible using the conservation of mass equation for  $C$  which is

$$\begin{cases} \partial_t C = -\nabla_0 \cdot (C V_f) & \text{in } \Omega_0 \\ V_f^\top N = 0 & \text{in } \partial\Omega_0 \end{cases} \quad (4.13)$$

Then, replacing 4.13 in 4.12 , and using 2.6, we have

$$\partial_t E = - \int_{\Omega_0} \mu \nabla_0 \cdot (C V_f) dV \quad (4.14)$$

$$= \int_{\Omega_0} C \nabla_0 \mu^\top V_f dV - \int_{\partial\Omega_0} C \mu V_f^\top N dS. \quad (4.15)$$

Since  $V_f^\top N = 0$ , the above expression reduces to

$$\partial_t E = \int_{\Omega_0} C \nabla_0 \mu^\top V_f dV \quad (4.16)$$

Finally, the Rayleighian is ready to be minimized. From 4.16,  $R$  is

$$R(C; V_f) = RT \int_{\Omega_0} C \nabla_0 \mu^\top V_f + \frac{\nu N_A}{2} C |V_f|^2 dV. \quad (4.17)$$

Then,  $\delta_{V_f} R = 0$  yields

$$c V_f = - \frac{RT}{\mu N_A} \nabla_0 C. \quad (4.18)$$

Plugging this into the balance of mass equation 4.13 finally gives the diffusion equation

$$\partial_t C = \frac{RT}{\nu N_A} \Delta_0 C. \quad (4.19)$$

## Chapter 5

# Modelling Hydrogels with the Onsager's Principle

### 5.1 Introduction

In the third chapter, of the basic relationships 2.13, 2.17, and 2.15, the last one was not used. Most importantly, it was not used explicitly the fact that the solvent has a certain velocity field  $V^f$ , which in general is different from  $V$  (the velocity of the network), and that their difference generates dissipation by viscous friction.

In this chapter, a variational model for hydrogels is developed using the Onsager's variational principle. Subsequently, the constitutive equations of the motion are obtained by minimizing the Lagrangian functional  $L$  with respect to the rate variables  $V$  and  $V^f$ .

*Remark.* The following notation is used for the following different time derivatives of a field  $u(x, t) = U(X, t)$  with  $x = \phi(X, t)$ .

- $\partial_t U(X, t) = \partial_t U(X, t)|_X$ , that is the Lagrangian time derivative of the field  $U(X, t)$  written with Lagrangian coordinates (Lagrangian time derivative means that  $X$  is fixed).
- $\partial_t u(x, t) = \partial_t u(x, t)|_x$ , that is the eulerian time derivative of the field  $u(x, t)$  written with eulerian coordinates (eulerian time derivative means that  $x$  is fixed).
- $D_t u(x, t) = \partial_t u(\phi(X, t), t)|_X$ , that it is the Lagrangian time derivative of the field  $u(x, t)$  written with eulerian coordinates.

Also, recall that for any field  $u(x, t)$ , the chain rule implies that

$$D_t u = \partial_t u + \nabla u \cdot v, \quad (5.1)$$

where  $v = \partial_t \phi(X, t)$  is the velocity field of the motion.

The premises of this model are the fundamental assumptions and formulas exposed in the second chapter. In particular, recall that we have the following fundamental equations:

- $1 + kC = J$  which is the molecular-incompressibility constraint, and  $k\partial_t C - JF^{-\top} : \nabla_0(V) = 0$  (its rate version).
- $C = Jc$  which links  $c$  and  $C$ .
- The conservation of mass for the solvent  $\partial_t c = -\nabla \cdot (cv^f) + r$  (also recall that  $r_0 = Jr$ ).

As previously discussed, there is dissipation when  $V \neq V^f$ . So, we define the *relative velocity* as  $V^r = V^f - V$ . This quantity will later be the fundamental ingredient for writing the dissipation potential and applying the Onsager's principle.

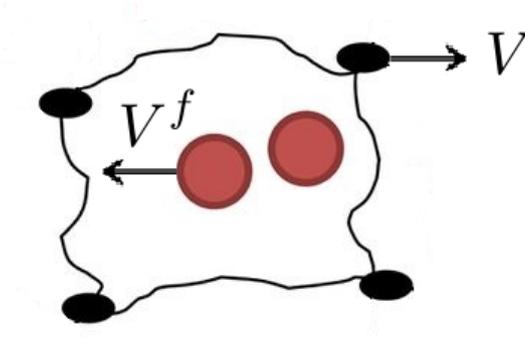


Figure 5.1: Dissipation arises when  $V^r := V^f - V \neq 0$ .

**Proposition 5.1.1.** *Consider the basic framework discussed in the second chapter. Then,  $C(X, t)$  satisfies*

$$\partial_t C = -JF^{-\top} : \nabla_0 \left( \frac{C}{J} V^r \right) + r_0. \quad (5.2)$$

*Proof.* Differentiating 2.13 yields

$$\partial_t C = JD_t c + c \partial_t J = JD_t c + CF^{-\top} : \nabla_0(V). \quad (5.3)$$

Let us compute  $D_t c$ . Recall that  $\nabla(c)v = \nabla \cdot (cv) - c\nabla \cdot (v)$ , so

$$D_t c = \partial_t c + \nabla c \cdot v = \partial_t c + \nabla \cdot (cv) - c\nabla \cdot (v).$$

Use that any field  $v(x, t) = V(X, t)$  satisfies  $\nabla \cdot (v) = F^{-\top} : \nabla_0(V)$ , to get

$$D_t c = \partial_t c + F^{-\top} : \nabla_0 \left( \frac{C}{J} V \right) - \frac{C}{J} F^{-\top} : \nabla_0(V).$$

Substitute this in 5.3 to obtain

$$\partial_t C = J \partial_t c + JF^{-\top} : \nabla_0 \left( \frac{C}{J} V \right).$$

Finally, use that  $\partial_t c = -\nabla \cdot (cv^f) + r$ , which is the balance of mass formula for the solvent in function of the eulerian molecular density  $c$ , and get

$$\begin{aligned} \partial_t C &= -J \nabla \cdot (cv^f) + Jr + JF^{-\top} : \nabla_0 \left( \frac{C}{J} V \right) \\ &= -JF^{-\top} : \nabla_0 \left( \frac{C}{J} (V^f - V) \right) + Jr, \end{aligned}$$

where 2.4 has been used again. Then, use that  $Jr = r_0$  and  $V^r = V^f - V$  so that the final result is

$$\partial_t C = -JF^{-\top} : \nabla_0 \left( \frac{C}{J} V^r \right) + r_0.$$

□

This new equation is the analogous of 2.13, but in this case the balance of mass is written in function of the Lagrangian molecular density  $C$ . Also, it must be noted that, contrary to the procedure used in the third chapter, such balance equations have been derived without invoking energetic considerations. The above proposition relies on the assumptions made in the second chapter and it is true regardless of further considerations over the energy of the system.

The above proposition has been obtained without using the constraint 2.17. Moreover, using 2.18 the rate form of the constraint can be written entirely in function of  $V$  and  $V^r$ . This is the analogous of what happened in 4.14: a process operator is used to write the Rayleighian as a function of the rate variables  $V$  and  $V^r$ . This fact is shown in the following corollary.

**Corollary 5.1.2.** *The motion is such that*

$$JF^{-\top} : \nabla_0 \left( V + k \frac{C}{J} V^r \right) - kr_0 = 0. \quad (5.4)$$

*Proof.* The result is found simply by using 2.18 and 5.2. As previously explained, now the term  $\partial_t C$  does not appear anymore in the constraint. □

*Remark.* Recall that, in general, every motion satisfies the identity

$$\nabla_0 \cdot (JF^{-\top}) = 0. \quad (5.5)$$

A proof can be found in [1]. This implies that for every vector field  $V$ ,

$$JF^{-\top} : \nabla_0(V) = \nabla_0 \cdot (JF^{-1}V). \quad (5.6)$$

**Corollary 5.1.3.** *Using the above remark, it is easy to see that*

$$\partial_t C = -\nabla_0 \cdot (CF^{-1}V^r) + r_0. \quad (5.7)$$

The expressions 5.2 and 5.7 are equivalent. Here, 5.6 has been used to go from one form to the other because in the paper [7] (which is exposed in Chapter 3), the balance of mass formula was written with the double contraction as 5.7. So, recalling the definition of  $\tilde{J}$  given in 3.2, we now have that

$$\tilde{J} = CF^{-1}V^r. \quad (5.8)$$

Moreover, in the model described in Chapter 3, it was shown that

$$\tilde{J} = -CM\nabla_0(\mu). \quad (5.9)$$

Therefore, according to that model,

$$V^r = -FM\nabla_0(\mu). \quad (5.10)$$

This equation relates the velocity  $V^r$  to the gradient of the chemical potential. Physically, it expresses the fact that the solvent moves *relatively* to the network in order to compensate to the difference in potential between different parts of the hydrogel. This is the interpretation of  $V^r$  according to the model developed in Chapter 3. In the next section, a similar relation between  $V^r$  and  $\mu$  will be found with the Onsager's principle.

## 5.2 The Lagrangian of the system

Now, we want to derive the equations of the motion using the Onsager's principle and the new quantity  $V^r$ . Let us fix the following physical quantities.

1. There is a body force  $B$  and a pumping function  $r_0$  acting on  $\Omega_0$ .
2. There is a fixed velocity  $V = \bar{V}$  on  $\Gamma_D$  and a prescribed traction  $PN = \bar{T}$  on  $\Gamma_N$  such that  $\Gamma_D \cup \Gamma_N = \partial\Omega_0$ .
3. There is a prescribed velocity  $V^r = \bar{V}^r$  on  $\Gamma_D^*$  and a prescribed chemical potential  $\mu = \bar{\mu}$  on  $\Gamma_N^*$  with  $\Gamma_D^* \cup \Gamma_N^* = \partial\Omega_0$ .

*Remark.* All the previous six conditions give rise to power. Nevertheless, since the Lagrangian  $L$  is minimized with respect to  $V$  and  $V^r$ , only the force  $B$ , the traction  $\bar{T}$  and the chemical potential  $\bar{\mu}$  will be relevant.

In order to apply the Onsager's principle, recall that the Lagrangian is,

$$L(\phi, C; V, V^r; \Pi) = \partial_t E + D + P + \mathbb{C}. \quad (5.11)$$

Let us see in detail these quantities.

- As we have previously seen, the free energy is

$$E[\phi, C] = \int_{\Omega_0} \left[ W^N(F) + W^S(C) \right] dV. \quad (5.12)$$

Then, from the chain rule and equation 5.2, we have

$$\begin{aligned} \partial_t E &= \partial_t \left( \int_{\Omega_0} \left[ W^N(F) + W^S(C) \right] dV \right) \\ &= \int_{\Omega_0} \left[ \frac{\partial W^N}{\partial F} : \partial_t F + \frac{\partial W^S}{\partial C} \partial_t C \right] dV \\ &= \int_{\Omega_0} \left[ \frac{\partial W^N}{\partial F} : \nabla_0(V) + \frac{\partial W^S}{\partial C} \left( r_0 - JF^{-\top} : \nabla_0 \left( \frac{C}{J} V^r \right) \right) \right] dV. \end{aligned}$$

- For writing  $\mathbb{C}$ , we use the constraint 5.4, so

$$\mathbb{C} = \int_{\Omega_0} \left[ -\Pi JF^{-\top} : \nabla_0 \left( V + k \frac{C}{J} V^r \right) + k \Pi r_0 \right] dV = 0 \quad (5.13)$$

- The external supplied power of the system is  $P = P^M + P^C$  where  $P^M$  is the mechanical power and  $P^C$  is the chemical one. Explicitly,

$$P^M = - \int_{\Omega_0} [B^\top V] dV - \int_{\Gamma_D} [T^\top \bar{V}] dS - \int_{\Gamma_N} [\bar{T}^\top V] dS \quad (5.14)$$

$$\begin{aligned} P^C &= - \int_{\Omega_0} [r_0 \mu] dV - \int_{\Gamma_D^*} [\mu C \bar{V}^r{}^\top F^{-\top} N] dS \\ &\quad - \int_{\Gamma_N^*} [\bar{\mu} C V^r{}^\top F^{-\top} N] dS. \end{aligned} \quad (5.15)$$

As previously explained, in  $P^M$  and  $P^C$ , the integrals with  $\bar{V}$ , and with  $\bar{V}^r$  can be ignored, because the functional  $L$  will be minimized with respect to  $V$  and  $V^r$ . So, they do not affect the solution.

The expression of  $P^C$  comes from using 5.7 with 3.4. Explicitly,

$$\begin{aligned} -P^C &= \int_{\Omega_0} \mu r_0 dV + \int_{\partial\Omega_0} \mu i dS \\ &= \int_{\Omega_0} \mu r_0 dV + \int_{\partial\Omega_0} \mu \tilde{J}^\top N dS \\ &= \int_{\Omega_0} [r_0 \mu] dV + \int_{\Gamma_D^*} [\mu C \bar{V}^r{}^\top F^{-\top} N] dS \end{aligned}$$

Also, in this case  $P^C$  is written with the minus sign with respect to the integrals, which is the opposite of what happened in equation 3.4 of Chapter 3. The reason is that the power  $P$  of Chapter 3 is the internally supplied power. Instead, the power  $P$  of this chapter is the externally supplied power.

- An intuitive way to model the dissipation is to say that it is quadratic in terms of  $V^r$ . So, we say that

$$D = \frac{1}{2} \int_{\Omega_0} \left[ CV^{r\top} \mathbb{D}V^r \right] dV. \quad (5.16)$$

Moreover, the matrix  $\mathbb{D}$  is symmetric and positive definite. This dissipation potential satisfies the requirements presented in Chapter 4. In fact,  $D$  is a convex with respect to  $V^r$ , it is nonnegative, and it clearly satisfies  $D(0) = 0$ .

Since the Lagrangian needs to be minimized with respect to  $V$  and with respect to  $V^r$ , we can decompose  $L$  in order to simplify the calculations. In fact,  $L$  is the sum of a functional  $L_1$ , which depends on  $V$  and does not depend on  $V^r$ , and another functional  $L_2$ , which depends on  $V^r$  and does not depend on  $V$ . In formulas,

$$L = L_1(\phi, C; V; \Pi) + L_2(\phi, C; V^r; \Pi), \quad (5.17)$$

with

$$\begin{aligned} L_1 = & \int_{\Omega_0} \left[ \nabla_0(V) : \left( \frac{\partial W^N}{\partial F} - \Pi J F^{-\top} \right) - V^\top B \right] dV \\ & - \int_{\Gamma_N} \left[ V^\top \bar{T} \right] dS + K_1(\phi, C; V^r; \Pi) \end{aligned} \quad (5.18)$$

and

$$\begin{aligned} L_2 = & \int_{\Omega_0} \left[ \frac{1}{2} CV^{r\top} \mathbb{D}V^r - \mu J F^{-\top} : \nabla_0 \left( \frac{C}{J} V^r \right) \right] dV \\ & - \int_{\Gamma_N^*} \left[ \bar{\mu} CV^r F^{-\top} N \right] dS \end{aligned} \quad (5.19)$$

where  $\mu = k\Pi + \frac{\partial W^S}{\partial C}$ .

This is just a way to simplify calculations because, with the above notation, it is clear that,

$$\operatorname{argmin}_V L(\phi, C; V, V^r; \Pi) = \operatorname{argmin}_V L_1(\phi, C; V; \Pi) \quad (5.20)$$

$$\operatorname{argmin}_{V^r} L(\phi, C; V, V^r; \Pi) = \operatorname{argmin}_{V^r} L_2(\phi, C; V^r; \Pi). \quad (5.21)$$

### 5.3 Minimizing the Lagrangian

Before minimizing the Lagrangian, consider the following useful definitions

$$\begin{aligned} \mathfrak{C}_D &= \{V : \Omega_0 \rightarrow \mathbb{R}^3 : V|_{\Gamma_D} = \bar{V}\} & \mathfrak{C}_0 &= \{W : \Omega_0 \rightarrow \mathbb{R}^3 : W|_{\Gamma_D} = 0\} \\ \mathfrak{C}_D^* &= \{V^r : \Omega_0 \rightarrow \mathbb{R}^3 : V^r|_{\Gamma_D^*} = \bar{V}^r\} & \mathfrak{C}_0^* &= \{W^r : \Omega_0 \rightarrow \mathbb{R}^3 : W^r|_{\Gamma_D^*} = 0\} \end{aligned}$$

We now minimize  $L$  with respect to  $V$  and  $V^r$ .

$\delta V$  : We look for a  $V \in \mathfrak{C}_D$  such that for every  $W \in \mathfrak{C}_0$ ,

$$\frac{d}{d\epsilon} L(V + \epsilon W) \Big|_{\epsilon=0} = 0 \quad (5.22)$$

Then, using equation 5.20, it is easy to see that

$$\begin{aligned} \frac{d}{d\epsilon} L(V + \epsilon W) \Big|_{\epsilon=0} &= \frac{d}{d\epsilon} L_1(V + \epsilon W) \Big|_{\epsilon=0} \\ &= \int_{\Omega_0} \left[ \nabla_0(W) : \left( \frac{\partial W^N}{\partial F} - \Pi J F^{-\top} \right) - W^\top B \right] dV \\ &\quad - \int_{\Gamma_N} \left[ W^\top \bar{T} \right] dS = 0. \end{aligned}$$

Then, put  $P = \partial W^N / \partial F - \Pi J F^{-\top}$ , to get that for every  $W$  test function

$$\begin{aligned} 0 &= \int_{\Omega_0} \left[ \nabla_0(W) : P - W^\top B \right] dV - \int_{\Gamma_N} \left[ W^\top \bar{T} \right] dS \\ &= \int_{\Omega_0} \left[ -W^\top \nabla_0 \cdot (P) - W^\top B \right] dV + \int_{\Gamma_N} \left[ W^\top P N - W^\top \bar{T} \right] dS \end{aligned}$$

where we have integrated by parts and used the fact that  $W|_{\Gamma_D} = 0$ . This yields the final system

$$\begin{cases} \nabla_0 \cdot (P) + B = 0 & \text{in } \Omega_0 \\ V = \bar{V} & \text{in } \Gamma_D \\ P \cdot N = \bar{T} & \text{in } \Gamma_N \end{cases} \quad (5.23)$$

$\delta V^r$  : We look for a  $V^r \in \mathfrak{C}_D^*$  such that for every  $W^r \in \mathfrak{C}_0^*$ ,

$$\frac{d}{d\epsilon} L(V^r + \epsilon W^r) \Big|_{\epsilon=0} = 0 \quad (5.24)$$

As before, using equation 5.21, we get

$$\begin{aligned} \frac{d}{d\epsilon} L(V^r + \epsilon W^r) \Big|_{\epsilon=0} &= \frac{d}{d\epsilon} L_2(V^r + \epsilon W^r) \Big|_{\epsilon=0} \\ &= \int_{\Omega_0} \left[ C W^{r\top} \mathbb{D} V^r - \mu J F^{-\top} : \nabla_0 \left( \frac{C}{J} W^r \right) \right] dV \\ &\quad - \int_{\Gamma_N^*} \left[ \bar{\mu} C W^r F^{-\top} N \right] dS = 0 \end{aligned}$$

where we have defined  $\mu = k\Pi + \frac{\partial W^S}{\partial C}$ .

Again, integrating by parts and using that  $\nabla_0 \cdot (JF^{-\top}) = 0$ , we have

$$0 = \int_{\Omega_0} \left[ CW^{r\top} (\mathbb{D}V^r + F^{-\top} \nabla_0(\mu)) \right] dV \\ + \int_{\Gamma_N^*} \left[ (\mu - \bar{\mu}) CW^r F^{-\top} N \right] dS.$$

This implies that

$$V^r = -\mathbb{D}^{-1} F^{-\top} \nabla_0(\mu). \quad (5.25)$$

Notice that we have also recovered the boundary condition on  $\Gamma_N^*$ .

Using this equation and 5.10, it is possible to derive the relationship between  $\mathbb{D}$  and  $M$ , which is the matrix defined in the model proposed in [7].

$$\mathbb{D}^{-1} = FMF^\top. \quad (5.26)$$

Also, the last system of equation is

$$\begin{cases} \partial_t C + JF^{-\top} : \nabla_0 \left( \frac{C}{J} V^r \right) = r_0 & \text{in } \Omega_0 \\ V^r = \bar{V}^r & \text{in } \Gamma_D^* \\ \mu = \bar{\mu} & \text{in } \Gamma_N^* \end{cases} \quad (5.27)$$

with  $V^r = -\mathbb{D}^{-1} F^{-\top} \nabla_0(\mu)$ .

So, the final results allows to define boundary conditions either on the the relative velocity  $V^r$  or on the chemical potential. Also, it possible to interchange the two quantities.

## 5.4 Conclusion

This model identifies the variational structure behind a nonlinear large deformations model for hydrogels. This variational structure can be the basis of new numerical methods that discretize directly the variational equation, instead of discretizing the PDE. Examples of such techniques can be found in [12]. Furthermore, Onsager's principle is a unique tool to couple multiple physics in soft matter. So, the proposed approach may be a starting point for developing more specific models in order to describe the physics of responsive hydrogels.

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