

THE SWELLING BEHAVIOR OF IONIC POLYMERS IN THE PRESENCE OF  
DIFFUSION AND CHEMICAL REACTIONS

A Dissertation

by

SEUNGIK BAEK

Submitted to the Office of Graduate Studies of  
Texas A&M University  
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 2003

Major Subject: Mechanical Engineering

THE SWELLING BEHAVIOR OF IONIC POLYMERS IN THE PRESENCE OF  
DIFFUSION AND CHEMICAL REACTIONS

A Dissertation

by

SEUNGIK BAEK

Submitted to Texas A&M University  
in partial fulfillment of the requirements  
for the degree of

DOCTOR OF PHILOSOPHY

Approved as to style and content by:

---

A. R. Srinivasa  
(Chair of Committee)

---

K. R. Rajagopal  
(Member)

---

T. Creasy  
(Member)

---

J. D. Humphrey  
(Member)

---

J. A. Weese  
(Head of Department)

May 2003

Major Subject: Mechanical Engineering

## ABSTRACT

The Swelling Behavior of Ionic Polymers in the Presence of Diffusion and Chemical Reactions. (May 2003)

Seungik Baek, B.S., Seoul National University

Chair of Advisory Committee: Dr. A. R. Srinivasa

During the past few decades, ionic polymers have attracted much attention due to their unique properties, i.e., a stimulus-sensitive swelling behavior. The use of ionic polymers in biotechnology and medicine is increasingly attractive for applications such as controlled drug delivery, biomimetic actuators, and chemical valves. The ability to model and predict the swelling behavior of polymers and mass flux with respect to external environmental conditions is very important in such applications.

The focus of this dissertation is on developing a continuum model for the behavior of a swollen solid and diffusion of a fluid through it in the presence of chemical reactions. To model diffusion through an ionic/nonionic polymer in the presence of mechanical deformation, we develop a variational procedure based on a thermodynamic framework for a swollen solid subject to constraints. This thermodynamic framework was mainly developed by Rajagopal and Srinivasa as a general thermodynamic framework for inelastic behavior of materials. First, a model for the mechanical behavior of a rubber-like solid in the presence of mass diffusion is developed using the variational procedure. By assuming a specific form for the Helmholtz potential function, we obtain an equilibrium equation that is identical to the equation suggested by Flory, Huggins, and Rehner. For the non-equilibrium problem, we assume a specific form for the rate of dissipation function and obtain the relation between pressure difference and mass flux. The numerical results show very good agreement

with experimental data for the diffusion of organic solvents through a rubber slab. Hysteresis response of the swollen solid due to time-dependent loads is also simulated by the model.

The variational procedure is also applied to pH-sensitive ionic polymers, which not only yields the equations for the deformation of a swollen solid and mass flux, but also the equations for chemical equilibrium. As a specific example, an anionic polymer containing carboxylic acid in a solution of NaOH is investigated and its behavior in solutions of different pH and surrounding pressures is predicted. The numerical results show good agreement with the experimental data.

To Jiyoung and Jonghwa

## ACKNOWLEDGMENTS

I would like to thank Professor Srinivasa for his support, encouragement and inspiration throughout the course of this work. I would like to express my appreciation to Professor Rajagopal for his invaluable teaching and encouragement for this work. I also would like to thank my friends and colleagues, Jaetaek Im, Minseok Ko, Parag Ravindran, Pradeep Hariharakumar, Krishna Kannan and Raguraman Kannan. I would finally like to thank my wife, Jiyoung, and my son, Jonghwa.

## TABLE OF CONTENTS

CHAPTER		Page
I	INTRODUCTION . . . . .	1
	A. Ionic polymers and their applications . . . . .	2
	1. Ionic polymers . . . . .	2
	2. Applications of ionic polymers . . . . .	4
	B. Objectives and specific issues involving modeling of ionic polymers . . . . .	10
	C. Outline of the dissertation . . . . .	11
II	LITERATURE REVIEW . . . . .	13
	A. Modeling of equilibrium swelling of polymers . . . . .	15
	B. Modeling of equilibrium swelling of ionic polymers . . . . .	19
	C. Modeling of the swelling behavior of polymers in the presence of mass flux . . . . .	20
	D. Modeling of the swelling behavior of polymers in the presence of mass flux and chemical reactions . . . . .	22
	E. Thermodynamic modeling of materials with dissipative processes . . . . .	25
III	VARIATIONAL PROCEDURE FOR EQUILIBRIUM STATE AND THE LIMIT OF CONSTRAINTS OF AN UNCON- STRAINED BODY . . . . .	27
	A. Preliminaries . . . . .	28
	1. Special assumptions on the configuration of a swollen solid in a fluid bath . . . . .	28
	2. Kinematics . . . . .	31
	B. Variational procedure for the equilibrium (or saturated) state	33
	1. Equilibrium of the unconstrained mixture . . . . .	35
	2. The volume additivity constraint as a limit of un- constrained body . . . . .	38
	C. The limiting procedure applied to thermomechanical constraints . . . . .	42
	1. Thermomechanical formulation for unconstrained thermoelasticity . . . . .	42

CHAPTER	Page
2.	Thermoelasticity with constraints . . . . . 45
a.	Deformation-temperature constraint as a limit of an unconstrained body . . . . . 46
b.	Deformation-entropy constraint as a limit of an unconstrained body . . . . . 49
c.	Deformation-energy constraint as a limit of an unconstrained body . . . . . 52
3.	The application of thermomechanical constraint to a rubberlike material . . . . . 56
D.	Conclusion . . . . . 65
IV	MODELING OF THE SWELLING BEHAVIOR OF A POLY- MER IN THE PRESENCE OF MASS FLUX . . . . . 66
A.	A special form for the Helmholtz potential and the re- sulting equilibrium swelling . . . . . 67
B.	Dissipative process in the swollen solid . . . . . 70
1.	Assumption of maximum rate of dissipation . . . . . 71
2.	The bulk dissipation and the saturation boundary condition . . . . . 71
C.	Diffusion of toluene through pure gum rubber sheet . . . . . 76
D.	Time dependent load and hysteresis . . . . . 82
E.	Conclusion . . . . . 96
V	OSMOTIC PRESSURE IN A SOLUTION . . . . . 97
A.	Osmosis and osmotic pressure . . . . . 97
B.	A specific Helmholtz potential and a derivation of os- motic pressure . . . . . 99
VI	MODELING OF THE SWELLING BEHAVIOR OF IONIC POLYMERS IN THE PRESENCE OF MASS FLUX AND CHEMICAL REACTIONS . . . . . 104
A.	Basic concepts of chemical reactions in solutions . . . . . 105
1.	Chemical reactions and chemical equilibrium . . . . . 105
2.	Acid and base solutions . . . . . 106
3.	Reactions in ionic solutions . . . . . 107
B.	Preliminaries . . . . . 109
C.	Ionization of an ionizable polymer network . . . . . 110



CHAPTER	Page
D. Variational procedure for the equilibrium state for an unconstrained ionic polymer . . . . .	113
E. The limit of constraints for unconstrained ionic polymers .	117
F. Dissipative processes . . . . .	119
G. Specific forms of the Helmholtz potential and the rate of dissipation functions . . . . .	121
H. Prediction of swelling behavior of anionic hydrogels . . . .	127
1. pH dependence of free swelling . . . . .	127
2. Diffusion through a membrane of an anionic hydrogel	136
I. Conclusion . . . . .	137
VII CONCLUSION . . . . .	140
REFERENCES . . . . .	141
APPENDIX A . . . . .	152
APPENDIX B . . . . .	156
VITA . . . . .	159

## LIST OF TABLES

TABLE		Page
I	Summary of constitutive relationships for unconstrained case . . . . .	45
II	Thermomechanical constraints and equivalent forms of potential energy functions . . . . .	56
III	Summary of equations for the diffusion of the fluid into the polymer .	74
IV	Representing variables and their usage . . . . .	111

## LIST OF FIGURES

FIGURE	Page
1	Equilibrium swelling of ionic gels vs. pH [3] . . . . . 2
2	Schematic structure of N-isopropylacrylamide- <i>co</i> -acrylic acid copolymer [18] . . . . . 3
3	Three designs for a pH-sensitive release system . . . . . 5
4	Model scheme and the principle of device type signal responsive drug delivery system using gel actuator (from Sutani <i>et al.</i> [27]) . . . 6
5	Schematics of a ionic polymer-metal composite(IPMC) artificial muscle and its actuation principle (from Shahinpoor and Kim [7]) . . 8
6	The system configuration: $\Omega_m$ is the region occupied by the swollen solid, $\Omega_f$ is the region occupied by the surrounding fluid. $\Gamma_f$ is the system boundary with outward normal $\mathbf{n}_2$ and pressure $P_\infty$ . $\Gamma_m$ is the fluid-solid interface with outward normal $\mathbf{n}_1$ and traction $\mathbf{t}$ specified in addition to that imposed by the fluid . . . . . 29
7	Volume expansion with temperature variation for different ambient pressures. Experimental data is from Wood and Martin [83] . . . 60
8	Comparison $C_p$ for $C_v = 1.662 \text{ kJ/kgK}$ , $C_p = 0 \text{ kJ/kgK}$ and data from Wood and Martin [83] . . . . . 61
9	The variation of temperature with axial stretch, for the different $C_v$ . Experimental data is from Dart (see James and Guth [84]) . . . 63
10	The variation of axial stress $\sigma$ with axial stretch, for the different $C_v$ 64
11	Free swelling for different values of $M$ (gm/mol) . . . . . 69
12	Schematic view of the current configuration for diffusion through a rubber sheet . . . . . 76

FIGURE	Page
13	Comparison of flux-pressure difference relations for toluene between (a) mixture theory 1: saturated boundary condition (Shi <i>et al.</i> [45]), (b) mixture theory 2: split traction boundary condition (Rajagopal and Tao [44]), (c) experimental data by Paul and Ebra-Lima [75], (d) current approach for the form of Helmholtz free energy (4.5) of mixture; $n=3$ , $\eta = 1$ , $\alpha = 9 \times 10^7$ dyne.day.gm/cc 79
14	Variation of volume fraction of solid through layer thickness for various values of pressure difference . . . . . 80
15	Comparison of numerical results with experimental results of Paul and Ebra-Lima [75] for toluene, o-xylene, and cyclohexane. The free energy function (4.5) is used here . . . . . 81
16	Schematic representation of a system with time dependent traction condition . . . . . 83
17	Volume change of the swollen polymer for the Step load 0.1 . . . . . 89
18	Volume change of the swollen polymer at release of the load from 0.1 to 0 . . . . . 90
19	The height change due to release of supplying load from 0.1, 0.2 and 0.3 to 0 . . . . . 91
20	Volume change at $Z=0$ under cyclic loading $F = 0.1 \times (1 - \cos(2\pi t/w))$ . Sharp peaks are shown up because of time steps of computation. . . . . 92
21	Volume change at $Z=0$ under cyclic loading $F = -0.1 \times \sin(2\pi t/w)$ . 93
22	Hysteresis of the deformation under cyclic loading $F = -0.1 \times \sin(2\pi t/w)$ 94
23	Hysteresis of the deformation under cyclic loading $F = -0.1 \times \sin(2\pi t/w)$ for different values of $w$ . . . . . 95
24	Schematic view of osmosis . . . . . 98
25	Schematic representation of lattice model. The circles P1, P2 and P3 represent molecules of P1, P2 and P3 pendant groups. The circles M1 and M2 represent molecules of mobile ions . . . . . 123

FIGURE	Page
26 Swelling ratio of pH-sensitive polymer vs. pH value of the solution (Dotted line shows the result from reduced equations (6.115), (6.116) and (6.117) ) . . . . .	130
27 Theoretical free swelling for different initial crosslink densities ( $\rho_o/M$ )	132
28 Theoretical free swelling for different pKa . . . . .	133
29 Theoretical swelling calculation. Experiments by Rička and Tanaka [38] for swelling in solutions of varying pH . . . . .	135
30 Flux and pressure difference relationships for a acrylic polymer at different pH values of the solution . . . . .	138

## CHAPTER I

### INTRODUCTION

During the past few decades, synthetic functional polymers have appeared and they respond in some desired way to the changes in temperature, pH, electric, magnetic field and so forth. These polymers are called ‘stimulus responsive’ or ‘smart’ polymers [1]. These changes are triggered by small changes in the environment but are apparent at the macroscopic level in the size and water content of the polymers. These macroscopic changes are reversible in the sense that the system returns to its initial state when the trigger is removed. Amongst the smart polymers, ionic polymers (polyelectrolytes) have attracted much attention due to their unique properties. One important property of polyelectrolytes is their ability to swell enormously in aqueous solutions depending on the electrostatic field generated by charged ions or by the surrounding electric/ magnetic sources. The swelling ratio of these polymers varies with respect to the external environmental conditions such as pH [2, 3] and temperature [4, 5]. Ionic polymers were increasingly attractive for many applications in biotechnology and medicine such as the controlled drug delivery [6], biomimetic actuators [7], gel robots [8], and chemical valves [9, 10].

Therefore, the ability to model and predict the mechanical behavior of ionic polymer is very important in such applications.

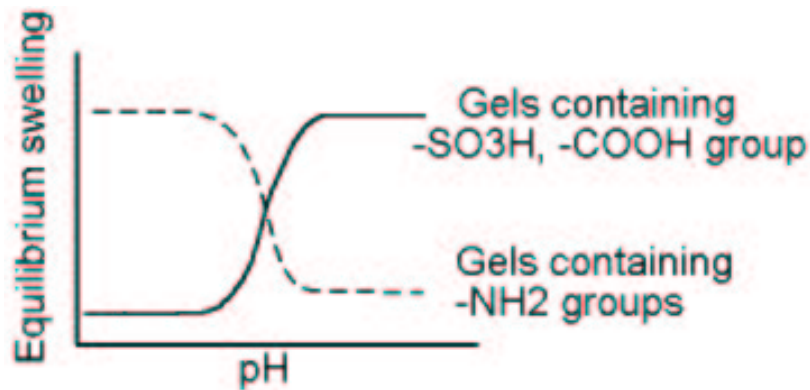


Fig. 1. Equilibrium swelling of ionic gels vs. pH [3]

## A. Ionic polymers and their applications

### 1. Ionic polymers

Ionic polymers are macromolecules having many ionizable groups (Oosawa [11]). They are also called polyelectrolytes, ionic gels, or ionic hydrogels. They dissociate into polyions and a large number of oppositely charged counter ions in a solution. Interactions between polyions and counter-ions causes phase transition [12, 13], change in diffusivity [14, 15, 16] and change in order of magnitude in equilibrium swelling [17, 2]. Typical examples of pH-sensitive polymers are polyacrylic acid, polymethacrylic acid (PMAA), poly(ethylene imine), and poly(N,N-dimethyl aminoethyl methacrylamide).

Ionic polymers can be divided to two classes by their pendant group: anionic polymeric networks containing acid pendant groups such as carboxylic or sulphonic acid pendant groups, and cationic polymeric networks containing base pendant groups such as amine groups. In both cases, their swelling behavior depends on the pH of the solution and their behavior are opposite to each other as shown in Figure 1 [3].

Copolymer gels consisting of N-isopropylacrylamide and acrylic acid are an example of ionic polymers. The schematic structure of the copolymer is shown in Figure

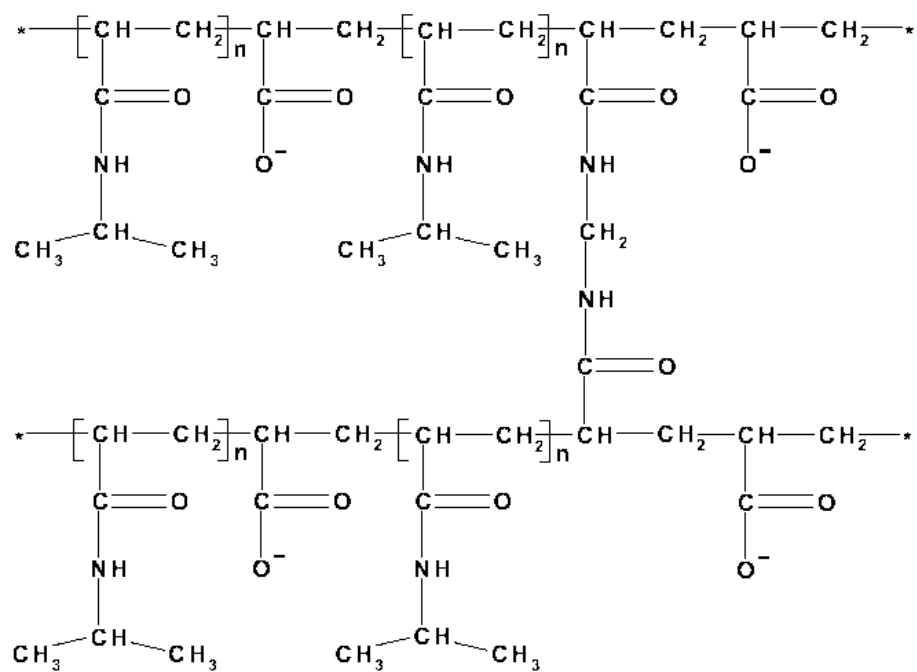


Fig. 2. Schematic structure of N-isopropylacrylamide-*co*-acrylic acid copolymer [18]



2 [18]. In a high pH solution, the carboxylic pendent group (-COOH) ionizes and the polymer swells or inflates absorbing the surrounding solution. In low pH, the carboxylic groups (-COO<sup>-</sup>) associate with H<sup>+</sup> and the polymer deflates. This copolymer can be used with glucose dehydrogenase as a glucose sensitive hydrogel [19, 20]. Glucose dehydrogenase catalyzes the conversion of neutral glucose into gluconic acid, accompanied by a decrease in pH. As a result, the repulsive forces are eliminated and the gel shrinks.

Usually, a volumetric deformation of an ionic polymer accompanies the diffusion of solutions through the polymer and its rate of deformation is very small. For example it takes a few hours to reach equilibrium swelling for the pH change [3, 21]. However, when the dimension of the structure is small and its motion does not associate to the diffusion of solutions, the speed of motion can be fast. A 1 mm diameter rod made of a cross-linked gel of poly(vinyl alcohol) chains entangled with polyacrylic-acid chains showed rapid electric-field-associated bending deformation; it bent to a semicircular shape within 1 sec [22]. Thus, the rate of deformation of ionic polymer structures may depend on the size of the structure and the process which the structure undergoes.

## 2. Applications of ionic polymers

This unique feature of ionic polymers allows them to be useful in various scientific and industrial applications such as controlled drug delivery systems [6, 20, 23], bio-sensor [24, 25], chemical valves [9, 10], and biomimetic actuators [26, 7, 8].

Among many fields in which pH-sensitive polymers have been successfully applied, the formulation of controlled drug delivery system is an interesting and actively studied area. In the human body, the pH variation is considerably large depending on the site. For example, the gastric pH is around 2 whereas intestinal pH is over

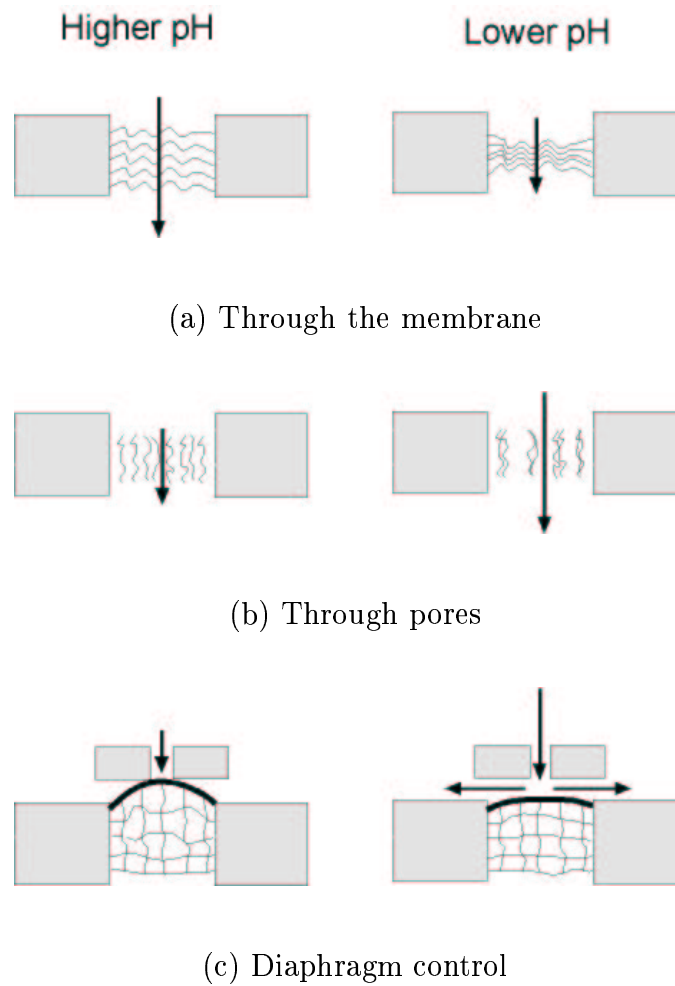


Fig. 3. Three designs for a pH-sensitive release system

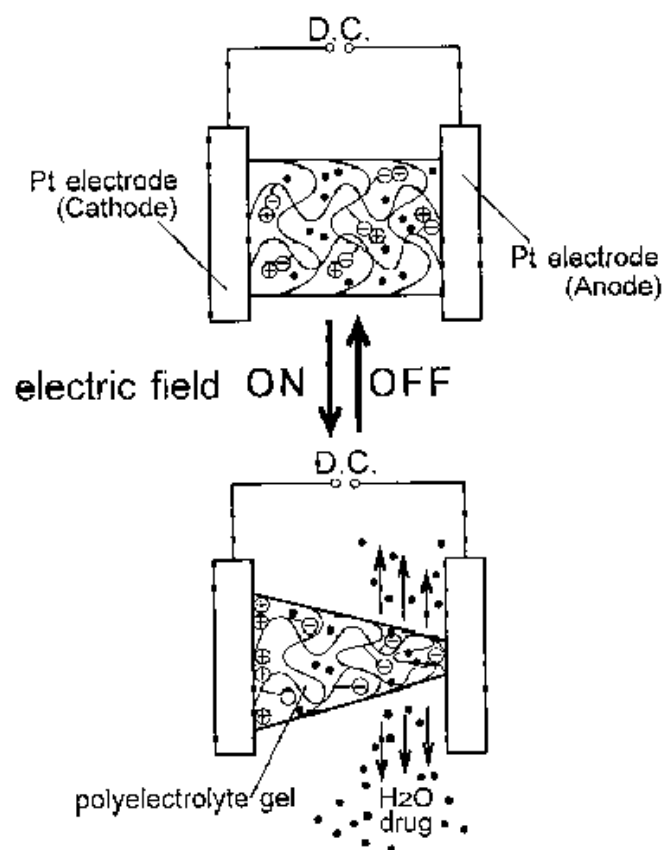
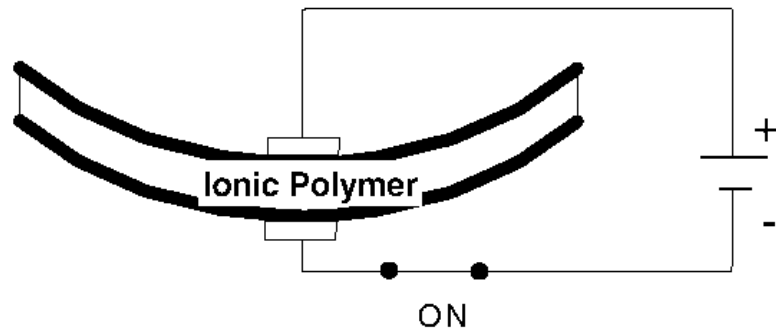


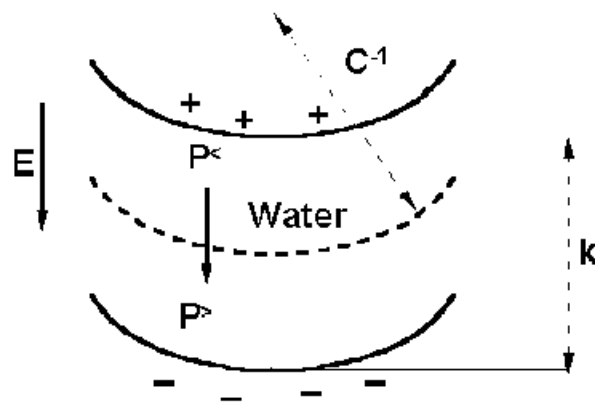
Fig. 4. Model scheme and the principle of device type signal responsive drug delivery system using gel actuator (from Sutani *et al.* [27])

7. Thus, using proper anionic or cationic pH-sensitive polymers, we can control the degree of swelling and the amount of drug delivered to the targeted site. Based on the above characteristic of the pH-sensitive polymer, Cao *et al.* [6] showed that three possible designs could be used as a switch to regulate the drug release. Figure 3 shows schematics of these designs. In the first design (Figure 3(a)), the switch is a pH-sensitive hydrogel. If the ionic polymer has acid pendant groups, in high pH, the ionic polymer swells so that the drug release rate increases. In low pH, a shrinkage of the polymer occurs, which decreases the membrane permeability, and hence the drug release rate. In the second design (Figure 3(b)), an ionic polymer is anchored to the pore of a pore-filled membrane. The ionic gel layer inside the pore expands and contracts with pH changes, which results in the opening and closing of channels in the pore to regulate the drug release rate. The third design uses a diaphragm as shown in Figure 3(c) to control the drug release rate. Cao *et al.* [6] designed a self-regulated drug delivery device using the third design scheme and they showed that the device can achieve a constant release rate by careful design of the shape of the drug reservoir, while a ionic polymer switch is used to regulate the drug release. Sutani *et al.* [27, 21] developed electro-responsive drug delivery device. The schematic picture of the device and its actuation principle is shown in Figure 4. They [28, 29] also synthesized a polymeric sensor and actuator of polyelectrolyte by UV and radiation polymerization and applied these to intelligent drug delivery systems.

Biological tissues are called charged tissue when their extracellular matrix is charged. Tissues are basically polymers and the charged tissues can be considered as ionic polymers. Articular cartilage, growth plate, intervertebral disc, and cornea are examples of charged tissues. Cartilage and cornea have fluid components diffused in fibrous networks of macromolecules; they are mainly composed of glycosaminoglycans (GAG), interstitial fluid, salts, glycoproteins and cells ([30]). The GAG has negatively



(a) Schematic view of an artificial actuator using an ionic polymer



(b) Actuation principle

Fig. 5. Schematics of a ionic polymer-metal composite(IPMC) artificial muscle and its actuation principle (from Shahinpoor and Kim [7])

charged pendant groups ( $\text{SO}_3^-$  and  $\text{COO}^-$ ) and the interactions between charged groups and mobile ions are primarily responsible for many macroscopically observed phenomena ([31]).

There have been attempts to mimic the motion of living organisms using ionic gels [1]. Shiga [22] designed an artificial fish with a gel tail and showed that the fish swam forward at a velocity of 2 *cm/s* as the gel oscillated under sinusoidally varied electric fields. A starfish shaped body and a beam shaped body were made of an anionic gel and it was manipulated by creating large bending motions [8]. Recently Shahinpoor and Kim [7] presented the fundamental properties and characteristics of ionic polymeric-metal composites (IPMCs) as biomimetic sensors, actuators and artificial muscles. A schematic diagram of the typical IPMC artificial muscle and its actuation principle is shown in Figure 5. The IPMC is composed of a perfluorinated ionic polymer layer, whose surfaces are coated by a conductive medium such as platinum. A strip of perfluorinated ionic membrane bends toward the anode under the influence of an electric potential. The water containing counterions moves toward anode and the motion of the actuator is created. These biomimetic actuators (jointless actuator) could be used in situations in which conventional machines consisting of rigid links and joints fail.

In applications of ionic polymers presented above, the change in the electro-chemical field causes the solid body to deform, which changes the diffusivity. Also the deformation of the body causes change in the distribution of fixed ionic charges and this results in the change of the electro-chemical field. Therefore, usually, the deformation field, mass flux, and chemical reaction are coupled with each other, and it will be advantageous to investigate the relation between the deformation of a swollen body, mass flux through the solid and chemical reaction simultaneously.

## B. Objectives and specific issues involving modeling of ionic polymers

The main objective of this work is to develop and investigate a mathematical model, which would make a suitable basis for the description of the mechanical behavior of swollen solid in the presence of mass flux through the body and electro-chemical changes. Typical examples of interest are the flux of organic liquids through a rubber membrane and a pH-sensitive ionic polymer in a solution. This investigation has these specific objective:

- To develop a model for the mechanical behavior of a swollen solid in the presence of mass flux and chemical reaction
- To solve a boundary value problem and compare the result with experiments and other theories

In order to develop the model, we use a thermodynamic frame work and derive governing equations and boundary conditions from two constitutive functions, namely, the Helmholtz potential and the rate of dissipation functions, rather than providing three separate equations for the deformation, diffusion and chemical equilibrium.

The specific issues that arise in modeling of swollen polymers are

- Interaction between deformation and mass flux
- Boundary conditions with regard to the mass flux
- Constraints and constraints responses

For the modeling of ionic polymers, the specific issues are

- Influence of electro-chemical environment on the swelling of the solid
- Influence of electro-chemical changes on the mass flux
- The role of osmotic pressure in the swelling of ionic polymers

### C. Outline of the dissertation

In chapter II, we review other theories in the literature. We review the Flory-Rehner equation and its extension to swollen ionic polymers. For the mechanical behavior of polymers in the presence of mass flux, mixture theory is reviewed. Extensions of mixture theory to include chemical reaction into its thermodynamic frame using stoichiometric coefficients are discussed. We also review the thermodynamic framework that we follow to model dissipative processes.

In chapter III, we develop a variational procedure for a swollen solid subject to mechanical constraints to obtain equations and boundary conditions for the equilibrium state. Basic assumptions on the configurations and thermodynamics are discussed. We first consider an unconstrained body and derive conditions for equilibrium state using a variational method. Then, we apply limiting procedure to the unconstrained body and find physical interpretations of constraint responses (such as the chemical potential). The limiting procedure is also applied to investigate three thermomechanical constraints (a deformation-temperature constraint, a deformation-energy constraint and a deformation-entropy constraint). In chapter IV, we derive a model for the diffusion of organic liquids through a rubber slab using the variational method based on the assumption of maximum rate of dissipation. The results are compared with the experimental data.

Before we directly extend the modeling procedure to ionic polymers, in chapter V, we investigate the idea of osmosis and osmotic pressure in the literature and, using the variational method presented in chapter III and a specific form of Helmholtz potential function for a simple system, we derive the expression for osmotic pressure. Then, in chapter VI, we develop a model for the swelling behavior of ionic polymers in the presence of mass flux and chemical reaction. Furthermore, using a specific



assumption on the dissipative behavior of materials, we derive field equations and boundary conditions for swollen solid, mass flux and chemical equilibrium. These results are applied to an anionic polymer in a base or acid solution, and the swelling behavior of the polymer and mass flux are numerically calculated for different pH and material parameters.

## CHAPTER II

### LITERATURE REVIEW

In this chapter we review other theories in the literature. We first present brief history of these theories, and then we review these theories by classifying (1) modeling of equilibrium swelling of polymers, (2) modeling of equilibrium swelling of ionic polymers, (3) modeling of swelling behavior of polymers in the presence of mass flux, (4) modeling of swelling behavior of polymers in the presence of mass flux and chemical reaction, and (5) thermodynamic modeling of materials with dissipative processes.

In the present work, we develop a model to predict the mechanical behavior of polymers in the presence of mass flux and chemical reaction. The basic requirement of this model is that it should well predict the swelling behavior of polymers without mass flux, i.e., equilibrium swelling behavior of ionic/non-ionic polymers. There were attempts to predict the equilibrium swelling behavior of solids based on the elasticity of the molecular network (see Treloar [32]). Flory examined a general form for the entropy change during the deformation of a polymer (see Flory [33]). Following this, the calculation of the entropy of a mixing fluid with a network polymer was worked out by Flory [34] and Huggins [35], which is known as the Flory-Huggins equation. Experiments agreed with the theory (Gee [36]). Flory and Rehner [37] derived equilibrium equation for cross-linked polymer.

For ionic polymers Flory [33] and Rička and Tanaka [38] used the concept of osmotic pressure (based on theoretical developments by Donnan [39]) as a swelling force and applied to the Flory-Rehner equilibrium equation. Brannon-Peppas and Peppas [2] followed the Flory's approach, but they related the osmotic pressure to the ionic strength of the solution. However, Katchalsky and Michaeli [40] criticized

the above approach and emphasized the role of the electrostatic force due to the charged ions in the swelling behavior of ionic polymer. Recently Ogawa *et al.* [41] presented an experiment which showed that the concept of osmotic pressure suggested by Flory is not adequate to predict the swelling behavior of ionic polymers.

The work by Flory and Treloar on swelling polymer in a solution was extended to model the relation between diffusion and swelling of polymers (Guo and Mackley [42], Peppas and Moynihan [43]). Gao and Mackley [42] suggested a generalized Fickian diffusion equation whose diffusion coefficient is related to the volume fraction of swollen polymer.

In general, the approach of Flory and Treloar provides models for the homogeneous swelling behavior of polymers in equilibrium. However, for the dissipative process due to the relative flow of fluid, mixture theory provides useful insight. Mixture theory was extended by Truesdell and it was further developed by many researchers to model mass flux through a mixture and its effect on the deformation of the mixture together (see Rajagopal and Tao [44]). Rajagopal, Wineman and their coworkers [45, 46, 47] solved boundary value problems for steady and unsteady diffusion of a fluid through solids undergoing large deformation. The behavior of chemical reacting mixtures with mass flux was investigated by Bowen [48], Nunziato and Walsh [49] and Drumheller [50].

In the present work, we follow a thermodynamic frame-work presented by Rajagopal and Srinivasa [51, 52] to model dissipative materials. So we briefly review the thermodynamic frame-work. Rajagopal and Srinivasa have presented the concept of multiple natural configurations and the assumption of maximum rate of dissipation. This thermodynamic frame-work was used to study many different phenomena, such as metal plasticity [52], twinning [53], shape memory alloys [54], viscoelastic fluids [55] and crystallization in polymers [56].

In the following sections, we review the literature in more detail by classifying them to (1) modeling of equilibrium swelling of polymers, (2) modeling of equilibrium swelling of ionic polymers, (3) modeling of swelling behavior of polymers in the presence of mass flux, (4) modeling of swelling behavior of polymers in the presence of mass flux and chemical reaction, and (5) thermodynamic modeling of materials with dissipative processes.

#### A. Modeling of equilibrium swelling of polymers

When a dry solid body (for example a dry natural rubber) is immersed in a fluid bath, the fluid diffuses through the solid body and the body gradually swells. Finally the swollen solid reaches an equilibrium state (saturated state). In the equilibrium state, there are two separated phases, a swollen solid phase and a surrounding fluid phase.

The equilibrium of a system is determined by the consideration that its free energy shall be a minimum with change in composition of the phases by mass flux across the interface. Based on this general assumption in thermodynamics, the concept of the *Gibbs free energy of dilution*,  $\Delta G$  has been introduced and it is assumed that  $\Delta G = 0$  at equilibrium. Treloar describes this with the following statement (Treloar [32, p. 124])

In the particular case in which the mixed phase is polymer plus liquid while the single phase is pure liquid, this means that the change in free energy on transferring a small quantity of liquid from the pure liquid phase to the mixed phase shall be zero. To represent this quantitatively, it is convenient to introduce the *Gibbs free energy of dilution* defined as the change in the Gibbs free energy of the system resulting from the transfer

of unit quantity of the system resulting from the transfer of unit quantity of liquid from the liquid phase to a very large quantity of the mixture.

The condition for equilibrium with respect to transfer of liquid is given by

$$\Delta G = 0. \quad (2.1)$$

The total free energy of dilution may be expressed in terms of the heat of dilution  $\Delta H$ , and the entropy of dilution  $\Delta S$ , i.e.,

$$\Delta G = \Delta H - T\Delta S. \quad (2.2)$$

The statistical estimations of  $\Delta H$  and  $\Delta S$  have been individually suggested by Flory [34] and Huggins [35], which resulted in the Flory-Huggins equation. Flory [34] considered the liquid and polymer molecules arranged on a three-dimensional lattice of sites such that each site may be occupied either by a liquid molecule or by a single segment of a polymer chain. Using a statistical treatment, he found the total number of distinguishable configurations and obtained the entropy of mixing  $S_m$  by the use of Boltzmann's relation as

$$S_m = -k \left[ n \ln \frac{n}{n + xN} + N \ln \frac{N}{n + xN} \right], \quad (2.3)$$

where  $n$ ,  $N$ , and  $x$  are the number of liquid molecules, the number of polymer molecules and the number of segments of one polymer, respectively. The entropy of dilution is obtained by differentiating (2.3) with respect to  $n$ , i.e.,

$$\Delta S = -R \left[ \ln(1 - \nu_s) + \left(1 - \frac{1}{x}\right) \nu_s \right], \quad (2.4)$$

where  $\nu_s$  is volume fractions of polymer in the swollen solid. To obtain the free energy of dilution, Flory [34] introduced an empirical equation for the heat of dilution,  $\Delta H$ ,

i.e.,

$$\Delta H = \alpha \nu_s^2, \quad (2.5)$$

Substituting the equations (2.4) and (2.5) into (2.2) leads to the following formula for the Gibbs free energy of dilution:

$$\Delta G = RT \left[ \ln(1 - \nu_s) + \left(1 - \frac{1}{x}\right) \nu_s + \frac{\alpha}{RT} \nu_s^2 \right]. \quad (2.6)$$

A similar form for  $\Delta G$  was also derived by Huggins [35] as

$$\Delta G = RT \left[ \ln(1 - \nu_s) + \left(1 - \frac{1}{x}\right) \nu_s + \chi \nu_s^2 \right], \quad (2.7)$$

where  $\chi$  is an adjustable parameter. The form (2.7) is known as the Flory-Huggins equation. If the polymer chain is sufficiently large, the equation (2.7) can be further reduced to

$$\Delta G = RT \left[ \ln(1 - \nu_s) + \nu_s + \chi \nu_s^2 \right] = 0. \quad (2.8)$$

Gee and Treloar [57] showed that the equation (2.8) agrees with data over the whole range of composition.

If the polymer is cross-linked, the Flory-Huggins equation is not sufficient to arrive at the free energy dilution. For the swelling of cross-linked polymers, Flory and Rehner [37] considered the configurational entropy of the network and expressed total free energy of dilution in the following form:

$$\Delta G = \Delta G_m + \Delta G_e, \quad (2.9)$$

where  $\Delta G_m$  is the free energy of dilution for an un-cross-linked polymer and  $\Delta G_e$  is the free energy change due to the elastic expansion of the network for a unit amount of liquid absorbed. By introducing the free energy change corresponding to the network

expansion [using a Gaussian network theory] as

$$\Delta G_e = \frac{\rho RT V_o}{M} \nu_s^{1/3} \quad (2.10)$$

and using  $\Delta G$  from the equation (2.8) for  $\Delta G_m$ , we obtain the free energy of dilution as

$$\Delta G = RT \left[ \ln(1 - \nu_s) + \nu_s + \chi \nu_s^2 + \frac{\rho V_o}{M} \nu_s^{1/3} \right], \quad (2.11)$$

where  $\rho$  is the density of the swollen solid,  $V_o$  is the molar volume of the fluid, and  $M$  is the molar weight between cross-links of the polymer. Therefore the condition for the equilibrium swelling becomes

$$\ln(1 - \nu_s) + \nu_s + \chi \nu_s^2 + \frac{\rho V_o}{M} \nu_s^{1/3} = 0 \quad (2.12)$$

Treloar [32] derived equations for more general cases of homogeneous strain. He assumed that the condition governing the equilibrium of a system which is operated on by external forces is that the change in the *Helmholtz free energy*  $\psi$  in a small displacement from equilibrium shall be equal to the work done by the applied forces, i.e.,

$$\delta\psi = \delta W \quad (2.13)$$

Furthermore he assumed that  $\delta G = \delta\psi$ . Then, on using the Flory-Huggins equation he derived the equation for the case of a simple hydrostatic pressure  $p$  (this pressure is not the pressure of the surrounding fluid but an additional pressure due to the traction on the surface of the swollen solid) in the following form:

$$\frac{\rho RT}{M} \nu_s^{1/3} + \frac{RT}{V_o} \left[ \ln(1 - \nu_s) + \nu_s + \chi \nu_s^2 \right] = -p. \quad (2.14)$$

In the present work, we will refer the above equation (2.14) as the ‘‘Flory-Rehner equation’’. Solving this equation, we can find a homogenous swelling value at equi-

librium under the additional traction on the swollen solid.

### B. Modeling of equilibrium swelling of ionic polymers

Flory [33] assumed that osmotic pressure arising from mobile ions is regarded as a swelling force due to ionic charges and by modifying equation (2.14), he suggested the equilibrium equation for the ionic polymer as

$$\frac{\rho RT}{M} \nu_s^{1/3} + \frac{RT}{V_o} \left[ \ln(1 - \nu_s) + \nu_s + \chi \nu_s^2 \right] = \pi_i, \quad (2.15)$$

where  $\pi_i$  represents osmotic pressure given by

$$\pi_i = RT \sum_i (C_i - C_{fi}), \quad (2.16)$$

where  $C_i$  and  $C_{fi}$  are molar concentrations of mobile ions inside polymer and molar concentrations of mobile ions in the surrounding fluid, respectively. The concentration of the mobile ions were obtained from a typical Donnan equilibrium (Donnan [39]). Rička and Tanaka [38] also used Donnan theory of swelling of weakly charged ion gels. They calculated osmotic pressure (2.16) by using an equilibrium equation for the ionic concentrations, which are given by

$$\frac{C_n}{C_{fn}} = 1, \quad \text{and} \quad \frac{C_i}{C_{fi}} = \exp\left(-\frac{z_i e U}{RT}\right), \quad (2.17)$$

where  $C_n$  and  $C_{fn}$  are concentrations of non-ionized components,  $z_i$ ,  $e$  and  $U$  are the valency of ions in the gel, the elementary charge and Donnan potential. Also, Brannon-Peppas and Peppas [2] and Okay and Durmaz [58] suggested the osmotic pressure in terms of the ionic strength and charge density of the swollen ionic polymer, respectively.

Originally, Flory [33] assumed that an electrostatic repulsion might tend to ex-



pand the network, but he assumed that mobile counterions in a solution reduce the electrostatic repulsions tremendously. As a result, he ignored the repulsive force from the equilibrium equation (2.18). However, Katchalsky and Michaeli [40] argued that the osmotic pressure assumed by Flory could not give even a rough approximation. They considered the electrostatic free energy based on the Debye-Hückel theory and they stated that the electrostatic force makes a significant contribution in polyelectrolytes and may not be ignored. Thus, the equilibrium equation may be given by (in the present terminology)

$$\frac{\rho RT}{M} \nu_s^{1/3} + \frac{RT}{V_o} \left[ \ln(1 - \nu_s) + \nu_s + \chi \nu_s^2 \right] = \pi_i - \frac{\partial \psi_e}{\partial V} \quad (2.18)$$

where  $\partial \psi_e / \partial V$  is the electrostatic force driven from the electrostatic potential  $\psi_e$ . Hasa *et al.* [59] extended Katchalsky and Michaeli's work and, considering the influence of charges on the deformation of the network, modified the elastic term of the equilibrium equation. The dependence of the Flory-Huggins interaction parameter,  $\chi$  in (2.18), on the volume fraction of the ionized polymer was also calculated by Ilavský *et al.* [60].

Recently, Ogawa *et al.* [41] tried to verify whether the concept of osmotic pressure due to mobile ions is adequate or not. They observed a strong effect of the charge distribution on the swelling of ionic gels. So, they concluded that their observation could no longer be explained in terms of the concept of osmotic pressure. Their experimental study strongly supports Katchalsky and Michaeli's work.

### C. Modeling of the swelling behavior of polymers in the presence of mass flux

When considering the actual diffusion of the fluid into the solid, the usual approaches using Fick's Law and Darcy's law are known to be insufficient (see Rajagopal and

Tao [44]) since they do not account for the swelling of the solid. The relation between diffusion and swelling of polymers was modeled by Guo and Mackley [42] and Peppas and Moynihan [43] by extending the work of Flory and Treloar. They generalized Fickian diffusion equation whose diffusion coefficient is related to the volume fraction of the swollen polymer. Truesdell reformulated and extended mixture theory and introduced local balance equations for mass, momentum, and energy of arbitrarily constituted mixtures (Truesdell and Toupin [61]). Following this, mixture theory was developed in its present form by many researchers through the 1960's and 1970's (see Bowen [62] and Atkin & Craine [63]). In 1966, Mills [64] used the volume fraction concept and the volume additivity condition for a mixture of two Newtonian fluids.

Mixture theory is based on the idea that particles of multiple constituents co-occupy any given point. This idea gave rise to great difficulty in the definition of "partial traction" and the prescription of the boundary conditions. Hence, there were few solutions to initial-boundary value problems within the context of mixture theory until early 1980's. An early attempt to study traction boundary value problems of a mixture of a solid infused with a fluid undergoing finite deformations was that by Shi, Rajagopal and Wineman [45]. They assumed that the boundary in contact with a pure fluid is saturated and the Flory-Rehner equation holds on the boundary. Later, Rajagopal, Wineman and Gandhi [65] suggested that the boundary of the fluid must be saturated so that the variation in the Gibbs free energy of dilution is zero. They also suggested that an investigation of the problem would entail the application of the tools of the calculus of variations to the minimization of the free energy functional and obtaining the natural boundary conditions. Various boundary value problems were solved with different boundary conditions by Gandhi, Rajagopal and Wineman [46] and Dai and Rajagopal [66]. Tao and Rajagopal [44] have developed a method of splitting the total traction on the boundary to obtain an additional boundary

condition without appealing to the saturation condition and have solved boundary value problems using this condition.

#### D. Modeling of the swelling behavior of polymers in the presence of mass flux and chemical reactions

The extension of mixture theory to include chemically reacting materials was given by Bowen [67, 48] and Nunziato and Walsh [49]. They related the mass interaction terms in the balance of mass to stoichiometry coefficients of the components and the number of moles of components. Nunziato and Walsh [49] studied the behavior of chemically reacting mixture using the notion of chemical equilibrium and some of the elements of stoichiometry (given by Bowen [67]) based on mixture theory. They used the mass concentration  $m_a$  of the  $a^{th}$  constituent

$$m_a = \frac{\rho_a}{\rho_R} |\det \mathbf{F}_a|, \quad (2.19)$$

where  $\rho_R$  is the reference density of the mixture and  $\mathbf{F}_a$  is the deformation gradient of motion of the  $a^{th}$  constituent. The mass interaction  $m_a^+$  is the mass change due to  $k$  independent chemical reactions and it is expressed as

$$m_a^+ = \rho_R M_a \sum_{\beta=1}^k s_\alpha^\beta \dot{r}_\beta, \quad (2.20)$$

where  $M_a$  is the molecular weight of  $a^{th}$  constituent,  $\dot{r}_\beta$  is the rate of  $\beta^{th}$  chemical reaction, and  $s_\alpha^\beta$  is the stoichiometry coefficient of  $\alpha^{th}$  constituent in  $\beta^{th}$  reaction. Since total mass is preserved in a reaction, we have

$$\sum_{\alpha} s_\alpha^\beta M_\alpha = 0, \quad \beta = 1, 2, \dots, N - R. \quad (2.21)$$

Based on the entropy inequality equation, they define the internal dissipation  $\xi$  and they assumed that the internal dissipation is minimum at the state of chemical equilibrium  $S^*$ . Let the mass interaction in chemical equilibrium be

$$(m_a^+)^* = \hat{m}_a^+(S^*) = 0. \quad (2.22)$$

For every arbitrarily small perturbation, the variation of the internal dissipation implies that

$$\sum_b \mu_b^* \left( \frac{\delta \hat{m}_b^+}{\delta m_a} \right)^* = 0, \quad (2.23)$$

where the chemical potential  $\mu_b$  is defined by

$$\mu_b = \frac{\partial \psi_b}{\partial m_b}. \quad (2.24)$$

Nunziato and Walsh call (2.23) *weak equilibrium states* in their remark on [49, p. 300]

Finally, we observe from (2.23) that the chemical potential  $\mu_a^*$ ,  $a = 1, 2, \dots, N$ , need not be all equal at equilibrium. In view of these results, the states characterized by (2.22) are called *weak equilibrium states*.

The states of thermochemical equilibrium are called *strong equilibrium states* if, in addition to (2.22), the chemical potentials  $\mu_a^*$ ,  $a = 1, 2, \dots, N$  are all equal:

$$\mu_a^* = \mu_b^*, \quad a \neq b, \quad a, b = 1, 2, \dots, N. \quad (2.25)$$

Then, they showed the relation of the strong equilibrium states (2.25) with the chemical affinity  $A_\beta$  (DeDonder [68]), which can be written as

$$A_\beta = - \sum_\alpha M_\alpha s_\alpha^\beta \mu_\alpha \quad (2.26)$$

Using (2.26) and (2.21), they pointed out that the strong equilibrium states (2.25) are sufficient to guarantee that the chemical affinities vanish in equilibrium. Furthermore, they concluded that every equilibrium state that is asymptotically stable is a strong equilibrium state in which the chemical potentials  $\mu_a$  all vanish.

However, the strong equilibrium states suggested by Nunziato and Walsh are too restrictive to serve as general equilibrium conditions for chemical reactions. Here, we find that they did not need to introduce the strong equilibrium states for chemical reactions. Indeed, the general chemical equilibrium condition (2.26) can be derived directly from the weak equilibrium states (2.23). To elaborate, we should remind that the mass interactions  $m_b^+$  and  $m_a$  can change only through a chemical reaction when the deformations of constituents are fixed. Thus, from (2.20),  $\delta m_b^+/\delta m_a$  can be written as

$$\frac{\delta m_b^+}{\delta m_a} = \frac{M_b s_b^\beta}{M_a s_a^\beta} \quad (2.27)$$

for the  $\beta^{th}$  reaction. Substituting (2.27) into the weak equilibrium state (2.23) gives

$$\sum_b \mu_b^* \frac{M_b s_b^\beta}{M_a s_a^\beta} = 0. \quad (2.28)$$

For the  $\beta^{th}$  reaction, the equation (2.28) implies that the chemical affinity of the  $\beta^{th}$  reaction vanishes at equilibrium, i.e.,

$$A_\beta = - \sum_b M_b s_b^\beta \mu_b^* = 0. \quad (2.29)$$

Therefore, without introducing the strong equilibrium state, we showed that the weak equilibrium state leads to a proper expression for chemical equilibrium. Later, Drumheller [50] reviewed the theories for reacting immiscible mixtures. However, the chemical reactions among the constituents of a mixture need to be investigated more within a thermodynamic frame for mixture theory, which would yield a general model

for various applications with chemical reactions.

Later, multiphase mixture theories such as triphasic theory (Lai *et al.* [69], Gu *et al.* [70], Mow *et al.* [31]) and quadriphasic mixture theory (Frijns *et al.* [71]) were applied to the swelling of polymeric biomaterials in an ionic solution. Lai *et al.* [70] assumed that articular cartilage in NaCl solution consists of three phases: solid, fluid and ionic phase and they investigated the interaction among the phases and the effects of applied osmotic pressure. However, they assumed that there is no chemical reaction between constituents so that the dissociation of ions due to change in electrostatic potential followed by the deformation could not be accounted for.

#### E. Thermodynamic modeling of materials with dissipative processes

Now, we review a thermodynamic frame work which make it possible to model the inelastic behavior of materials by specifying the way the energy is stored and dissipated.

Amongst all possible processes, the process that is chosen is one that maximizes the rate of dissipation, provided it meets the system equation for the dissipative process and any other constraints. This assumption is called the assumption of the maximum rate of dissipation. This assumption was introduced by Ziegler [72] and developed by Rajagopal and Srinivasa [52] to model the behavior of inelastic materials. Ziegler [72, p. 135] stated the principle of maximum rate of entropy production as

The principle of maximum rate of entropy production may be considered as a more precise version of the second fundamental law and seems particularly suggestive. In fact, if a closed system tends towards its state of maximum entropy, it does not seem unreasonable to postulate that, in a stable system subjected to prescribed irreversible forces, the rate of

entropy increase be a maximum, i.e., that the system should approach its final state on the shortest possible way.

This statement shows the physical idea behind the assumption. The rate of dissipation is the same as the product of the absolute temperature and the entropy production in an isothermal process. Rajagopal and Srinivasa [52] developed the assumption of maximum rate of dissipation criterion and presented preliminary consequences of the assumption. The maximum rate of dissipation assumption provides a simple, physically reasonable way to obtain the evolution equations without introducing other new balance laws or new concepts of internal forces.

Rajagopal and Srinivasa ([73] and [51]) have introduced also the notion of multiple natural configurations. The concept of multiple natural configuration and the assumption of maximum rate of dissipation was used to study many different phenomena, such as metal plasticity [52], twinning [53], shape memory alloys [54], viscoelastic fluids [55] and crystallization in polymers [56]. In fact, the theory for materials with multiple natural configurations make it possible to model both elastic behavior and inelastic behavior of materials by specifying the way the energy is stored and dissipated. We will utilize the assumption of global maximum rate of dissipation to derive field equations and boundary conditions.

## CHAPTER III

VARIATIONAL PROCEDURE FOR EQUILIBRIUM STATE AND THE LIMIT  
OF CONSTRAINTS OF AN UNCONSTRAINED BODY

In this chapter, we present a variational procedure for a swollen solid in equilibrium state and a technique for dealing with constraints. This procedure is applied to a closed system consisting of a swollen solid and a surrounding fluid (see figure 6) and not only governing equations and boundary conditions of the system but also interface conditions between the swollen solid and the surrounding fluid in the equilibrium state are obtained. We first assume that the swollen solid and the surrounding fluid is unconstrained. Then, we apply a limiting process to the unconstrained bodies and find the physical interpretations of constraint responses for the volume additivity constraint in the swollen solid and the incompressibility constraint in the surrounding fluid. Furthermore, this limiting procedure is applied to three classes of thermomechanical constraints for a thermoelastic body (a deformation-temperature constraint, a deformation-energy constraint and a deformation-entropy constraint) and reveals some useful facts about the thermomechanical constraints in thermoelasticity.

We consider the equilibrium of a swollen solid immersed in a fluid bath (for example a polymer immersed in a toluene). We treat the response of the swollen solid as that of a single continuum in the presence of mass diffusion. In some ways the procedure is similar to the consideration of the thermomechanics of solids in the presence of thermal diffusion. Thus, the basic structure of the theory is akin to Treloar's considerations. We should note that this approach is *not mixture theoretic* in the sense that we do not postulate the existence of two different media, each with their own balance laws. For understanding of the thermodynamics and the variational procedure for equilibrium state, we find two major stumbling blocks. The first is the



presence of mechanical constraints (incompressibility of the fluid and the volume additivity constraint for the fluid-solid mixture) which prevents the identification of the proper chemical potential associated with the diffusion of the fluid. The second is the fact that the swollen solid is an open system (since the fluid is allowed to diffuse freely into and out of the boundary of the swollen solid) and hence the validity of the process of minimization of the free energy of the mixture alone is unclear.

We overcome the first problem by first considering an equilibrium of a compressible fluid and a compressible solid and then obtaining that for the incompressible fluid and the volume additivity constraint by a limiting process akin to the one described by Ogden [74] for the case of incompressible rubber elasticity. The second difficulty is overcome by considering the equilibrium on not just the swollen solid but encompassing the fluid bath as part of the system. Then the boundary of the swollen solid becomes an internal interface of the system while the global system remains closed. We not only recover Treloar's results for the stress in the solid, but also our considerations enable the identification of the interface conditions between the fluid and the solid in the presence of the volume additivity constraint.

## A. Preliminaries

### 1. Special assumptions on the configuration of a swollen solid in a fluid bath

Let us consider an ideal network polymer which is homogeneous and incompressible in the dry state. This solid is immersed in a fluid bath. The fluid surrounding the solid diffuses into the solid and as a result the solid gradually swells. Also when the swollen solid is squeezed, the fluid diffuses out from the swollen solid and the volume of the swollen solid decreases. From this observation, Treloar [32] pointed out that the swollen solid corresponds to a compressible material made up of a single constituent

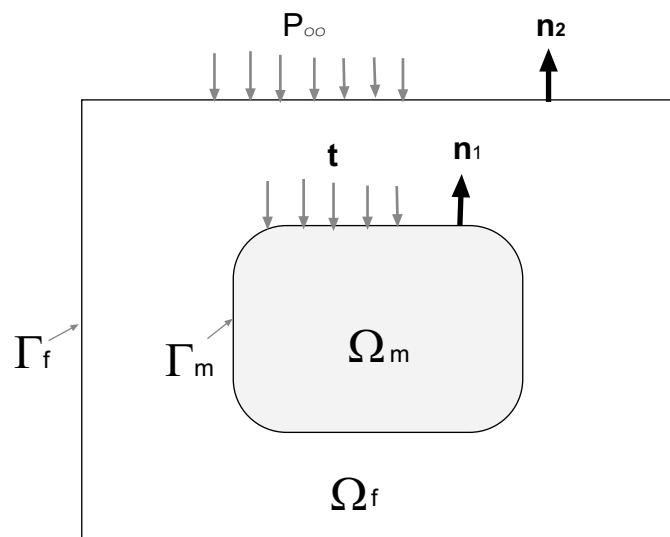


Fig. 6. The system configuration:  $\Omega_m$  is the region occupied by the swollen solid,  $\Omega_f$  is the region occupied by the surrounding fluid.  $\Gamma_f$  is the system boundary with outward normal  $\mathbf{n}_2$  and pressure  $P_\infty$ .  $\Gamma_m$  is the fluid-solid interface with outward normal  $\mathbf{n}_1$  and traction  $\mathbf{t}$  specified in addition to that imposed by the fluid

with regard to its mechanical properties, even though the solid in the dry state and the fluid may be treated as incompressible.

In the present work, we follow Treloar's approach and treat the swollen solid as a compressible solid whose mass is allowed to change with its compressibility arising from mass diffusion. In the subsequent discussion, the term "swollen solid" represents the compressible solid (an idealized single continuum) and by a saturated solid we mean the one which has swollen to the maximum extent possible. Since we now have diffusional motion between the solid and fluid, we need to carefully define the notion of position, velocity etc. of the swollen solid. Here, since the polymer network has a "backbone" structure, it is natural to follow this structure and define position, velocity etc. utilizing this backbone. We assume that we can follow the particle of the solid constituent in the swollen solid. Then, we set the position of the solid constituent as the position of the swollen solid (the idealized single continuum).

The density of a swollen solid is the mass of the swollen solid per unit volume. Note that the density of the swollen solid is neither the density of the solid constituent alone nor the density of the fluid constituent, but the total mass of the solid constituent and the fluid constituent per the unit volume. The current density of the swollen solid can change due to the deformation of the swollen solid and mass flux (mass diffusion). Here the mass flux is not treated as the flux of new particles but (somewhat akin to heat flux) is simply regarded as a contributing term to the mass balance. Hence this mass flux does not carry momentum.

This approach is a dramatic simplification and is quite different from the fundamental assumptions of the theory of mixtures. Also, this approach is appropriate when the mass flux is much slower than the wave propagation of a fluid. For example, let us consider a diffusion of toluene through a rubber slab (for experimental data, see Paul and Ebra-Lima [75]). The experimental data shows that the volume

flux of toluene through a rubber slab with 0.0265 cm thickness is approximately 10  $cc/cm^2$  day under a pressure difference of 500 psi ( $3.4 \times 10^7$  dynes/ $cm^2$ ). We can also calculate a inertial force which is required to accelerate the same amount of toluene from the velocity 0 to 10  $cm/day$  through the distance of 0.0265 cm. The inertial force is calculated approximately  $3.9 \times 10^{-7}$  dynes, which is much smaller than that of diffusion. Thus, in this example, we may ignore the inertial effect.

## 2. Kinematics

Let the unswollen, unstrained body in the dry state occupy a configuration  $\kappa_o$  initially (see figure 6). This is then immersed in a fluid bath and it gradually deforms with time both due to the force of the fluid on its boundary as well as due to the gradual infusion of the fluid. Let the swollen body, immersed in a fluid bath, occupy a configuration  $\kappa_t$  at time  $t$ . Let  $\Omega_m$  and  $\Omega_f$  represent the regions of Euclidean space occupied by the swollen body and the surrounding fluid, respectively. The motion measured from a reference configuration  $\kappa_o$ , the displacement and deformation gradient of the fluid infused body are given respectively by

$$\mathbf{x}_m = \chi_{\kappa_o}(\mathbf{X}_m, t), \quad \mathbf{u}_m = \mathbf{x}_m - \mathbf{X}_m, \quad \mathbf{F} = \frac{\partial \chi_{\kappa_o}}{\partial \mathbf{X}_m}, \quad (3.1)$$

where  $\mathbf{X}_m$  and  $\mathbf{x}_m$  are the position of a particle in the body in  $\kappa_o$  and  $\kappa_t$  respectively. The motion  $\mathbf{x}_f$  and displacement  $\mathbf{u}_f$  of fluid are defined in the same way as that of the mixture region. It should be emphasized that  $x_f$  and  $u_f$  does not correspond to the motion of the fluid in the swollen body but only that of the fluid surrounding the swollen solid, i.e., the region  $\Omega_f$  in Figure 6.

The velocity of the swollen solid is given by

$$\mathbf{v} = \frac{\partial \chi_{\kappa_o}}{\partial t} \Big|_{\text{fixed } \mathbf{x}}. \quad (3.2)$$

The densities of the swollen solid and the fluid at time  $t$  are  $\rho_m$  and  $\rho_f$  respectively, while  $\rho_{mo}$  and  $\rho_{fo}$  denote the densities of the mixture and the fluid at the initial configuration. In the subsequent developments, since the boundary of the swollen body is not a material boundary (since the fluid can diffuse in and out of it) we shall write the balance laws etc. in spatial notation. Since the change of mass of the swollen solid is equal to the amount of the mass flux of the fluid through the boundary of the swollen solid, the equations of the conservation of mass for the mixture region  $\Omega_m$  reduces to

$$\frac{\partial \rho_m}{\partial t} + \operatorname{div}(\rho_m \mathbf{v}_m) + \operatorname{div} \mathbf{q} = 0, \quad \text{in } \Omega_m \quad (3.3)$$

where  $\mathbf{q}$  denotes the mass flux through the swollen solid. The notation  $\partial(\cdot)/\partial t$  represents a time derivative at a fixed location and the notation  $\operatorname{div}(\cdot)$  stands for the divergence operator with respect to the spatial variables.

The equation of the concentration of mass for the region of the surrounding fluid  $\Omega_f$  is given by

$$\frac{\partial \rho_f}{\partial t} + \operatorname{div}(\rho_f \mathbf{v}_f) = 0, \quad \text{in } \Omega_f \quad (3.4)$$

where  $\mathbf{v}_f$  denotes the velocity of surrounding fluid.

An assumption commonly used for mixture problems is the volume additivity constraint (Mills [64], Rajagopal and Tao [44]) representing the fact that the current volume of the swollen rubber is the sum of the volumes of the original unswollen rubber and the volume of the fluid absorbed. By considering a homogeneously swollen body, we can then deduce that

$$\rho_m V_m = \rho_{mo} V_{mo} + \rho_{fo} (V_m - V_{mo}) \quad (3.5)$$

where  $V_m$  and  $V_{mo}$  are the volume of the solid in the current swollen state and the

initial unswollen state. Dividing (3.5) by  $V_m$  we get

$$\rho_m = \rho_{fo} + \frac{\rho_{mo} - \rho_{fo}}{J}, \quad \left( J = \frac{V_m}{V_{mo}} = \det \mathbf{F} \right) \quad (3.6)$$

Typically the above equation is used a local internal constraint restricting the motion of the material. However, as the constraint obscures many of the thermodynamical features essential to the understanding of the behavior of the material, we shall not invoke this constraint a-priori. Rather we shall develop the theory *without* the use of this constraint and then by means of a limiting process, obtain the relevant equations for the constrained material. In order to demonstrate the validity of the above approach, we rederive the equations with the use of a Lagrange multiplier technique and show that the resulting equations are the same. In order to accomplish this, we shall need a new variable  $\phi$ , defined as

$$\phi = \rho_m - \rho_{fo} - \frac{\rho_{mo} - \rho_{fo}}{J}. \quad (3.7)$$

The vanishing of  $\phi$  corresponds to the volume additivity limit.

#### B. Variational procedure for the equilibrium (or saturated) state

Let us consider an equilibrium state of a closed system in sense that the matter does not enter or leave across the boundary of the system. In the closed system consisting of the swollen solid and the surrounding fluid, the change in the internal energy of system  $\delta\varepsilon$  is equal to the work done on the system  $\delta W$  and the heat transferred  $\delta Q$ , i.e.

$$\delta\varepsilon = \delta W + \delta Q \quad (3.8)$$

and assuming that the deformation is reversible and the absolute temperature  $\theta$  is constant during the process, we get the relation

$$\delta Q = \theta \delta \eta \quad (3.9)$$

where  $\eta$  is the entropy. Since the Helmholtz free energy is defined as  $\Psi = \varepsilon - \theta \eta$ , substituting this into (3.8) and using (3.9) results in

$$\delta \Psi = \delta W. \quad (3.10)$$

Callen [76, p. 159] states this result as:

The work delivered in a reversible process, by a system in contact with a thermal reservoir, is equal to the decrease in the Helmholtz potential of the system.

In the problem of a swollen solid immersed in a fluid, the equilibrium state has been interpreted as the body reaches its saturated state, so that the body in such a saturated state cannot be diluted further and cannot absorb any additional fluid (see Tao and Rajagopal [47]).

Now, we consider the problem of the swollen body that is in equilibrium with the surrounding liquid (see figure 6). In order to elucidate the physical interpretations of the terms that appear in the governing equations, we shall assume that the fluid as well as the body are compressible. Thus, let us assume that the swollen solid and the fluid are characterized by specific Helmholtz free energy *per unit current volume* of the swollen solid and the surrounding fluid of the form respectively of the form

$$\psi_m = \hat{\psi}_m(\mathbf{F}, \rho_m), \quad \psi_f = \hat{\psi}_f(\rho_f). \quad (3.11)$$

Then, the total Helmholtz free energy  $\Psi$  is obtained by integrating the two functions over  $\Omega_m$  and  $\Omega_f$ .

$$\Psi = \int_{\Omega_m} \psi_m dV + \int_{\Omega_f} \psi_f dV. \quad (3.12)$$

Now assume that known tractions in excess of the pressure of the fluid are applied on the boundary of the swollen solid. In the presence of this traction, the fluid permeates the solid and the swollen solid reaches the saturated state. This is the problem addressed by Treloar [32], who considered a constant compressive stress on the boundary of the swollen body and minimized the free energy of the swollen body alone. Furthermore, he anticipated the final result and assumed that the body is homogeneously deformed. We however follow a longer and more formal path and minimize the free energy functional (3.12) of the combined system consisting of the swollen solid as well as the surrounding fluid, for given tractions on the boundary of the swollen polymer and the boundary of the fluid (see Figure 6). This ensures that the boundary of the entire system (swollen solid and surrounding fluid) is a material surface that is a so-called diathermal wall so that the temperature is maintained constant.

### 1. Equilibrium of the unconstrained mixture

Let us assume that the fluid is subject to a pressure  $P_\infty$  on its external boundary and an additional traction  $\mathbf{t}$  is specified on the on the boundary of the swollen polymer. Thus, we extremize  $\Phi := \left( \Psi - \int_{\Gamma_m} \mathbf{t} \cdot \mathbf{u}_m dA + \int_{\Gamma_f} P_\infty \mathbf{n}_2 \cdot \mathbf{u}_f dA \right)$  over the set of kinematically admissible displacements of the swollen solid and the fluid, i.e., we set  $\delta\Phi = 0$ . In order to do this we need to calculate the variation of the Helmholtz



potential  $\delta\Psi$ . A routine calculation leads to

$$\begin{aligned}\delta\Psi &= \int_{\Omega_m} \delta\psi_m dV + \int_{\Gamma_m} (\psi_m - \psi_f) \delta\mathbf{u}_m \cdot \mathbf{n}_1 dA \\ &+ \int_{\Omega_f} \delta\psi_f dV + \int_{\Gamma_f} \psi_f \delta\mathbf{u}_f \cdot \mathbf{n}_2 dA\end{aligned}\quad (3.13)$$

Each term in the above equation is expanded by using the chain-rule and the conservation of mass, (3.3) and (3.4), to obtain

$$\begin{aligned}\delta\psi_m &= \frac{\partial\psi_m}{\partial\mathbf{F}} \cdot \delta\mathbf{F} + \frac{\partial\psi_m}{\partial\rho_m} \delta\rho_m \\ &= \frac{\partial\psi_m}{\partial\mathbf{F}} \cdot (\text{grad}(\delta\mathbf{u})\mathbf{F} - \text{grad}(\mathbf{F})\delta\mathbf{u}) - \frac{\partial\psi_m}{\partial\rho_m} (\text{div}(\rho_m\mathbf{v}_m) + \text{div}\mathbf{q}) \\ &= \frac{\partial\psi_m}{\partial\mathbf{F}} \mathbf{F}^T \cdot \text{grad}\delta\mathbf{u}_m - \text{grad}\psi_m \cdot \delta\mathbf{u}_m - \frac{\partial\psi_m}{\partial\rho_m} (\rho_m \text{div}\delta\mathbf{u}_m + \text{div}\delta\mathbf{q})\end{aligned}\quad (3.14)$$

and

$$\delta\psi_f = \frac{\partial\psi_f}{\partial\rho_f} \delta\rho_f = -\text{grad}\psi_f \cdot \delta\mathbf{u}_f - \rho_f \frac{\partial\psi_f}{\partial\rho_f} \text{div}\delta\mathbf{u}_f \quad (3.15)$$

Substituting (3.14) and (3.15) into (3.13), and using the divergence theorem, the variation of total stored energy is obtained as

$$\begin{aligned}\delta\Psi &= \int_{\Omega_m} \left( \left[ -\text{div}\left(\frac{\partial\psi_m}{\partial\mathbf{F}}\mathbf{F}^T\right) - \text{grad}\psi_m + \text{grad}\left(\rho_m \frac{\partial\psi_m}{\partial\rho_m}\right) \right] \cdot \delta\mathbf{u}_m \right. \\ &\quad \left. + \text{grad}\left(\frac{\partial\psi_m}{\partial\rho_m}\right) \cdot \delta\mathbf{q} \right) dV \\ &+ \int_{\Omega_f} \left( \left[ -\text{grad}\psi_f + \text{grad}\left(\rho_f \frac{\partial\psi_f}{\partial\rho_f}\right) \right] \cdot \delta\mathbf{u}_f \right) dV \\ &+ \int_{\Gamma_m} \left( \left[ \mathbf{F}\left(\frac{\partial\psi_m}{\partial\mathbf{F}}\right)^T + \left(\psi_m - \rho_m \frac{\partial\psi_m}{\partial\rho_m} - \psi_f + \rho_f \frac{\partial\psi_f}{\partial\rho_f}\right)\mathbf{I} \right] \delta\mathbf{u}_m \right. \\ &\quad \left. + \left[ \frac{\partial\psi_f}{\partial\rho_f} - \frac{\partial\psi_m}{\partial\rho_m} \right] \delta\mathbf{q} \right) \cdot \mathbf{n}_1 dA \\ &+ \int_{\Gamma_f} \left[ \psi_f - \rho_f \frac{\partial\psi_f}{\partial\rho_f} \right] \delta\mathbf{u}_f \cdot \mathbf{n}_2 dA\end{aligned}\quad (3.16)$$

then, by the usual procedure of the calculus of variations, we arrive at the differential equation that characterizes the equilibrium configuration of the system in the form

$$\operatorname{div}(\hat{\mathbf{T}}) = \mathbf{0} \quad \text{in } \Omega_m \quad (3.17)$$

$$\operatorname{grad}\left(\frac{\partial\psi_m}{\partial\rho_m}\right) = 0 \quad \text{in } \Omega_m \quad (3.18)$$

$$\operatorname{grad}\left(\rho_f\frac{\partial\psi_f}{\partial\rho_f} - \psi_f\right) = 0 \quad \text{in } \Omega_f \quad (3.19)$$

where

$$\hat{\mathbf{T}} = \frac{\partial\psi_m}{\partial\mathbf{F}}\mathbf{F}^T - \left(\rho_m\frac{\partial\psi_m}{\partial\rho_m} - \psi_m\right)\mathbf{I}, \quad (3.20)$$

together with the natural boundary conditions

$$\hat{\mathbf{T}}\mathbf{n}_1 = \mathbf{t} - \left(\rho_f\frac{\partial\psi_f}{\partial\rho_f} - \psi_f\right)\mathbf{n}_1 \quad \text{on } \Gamma_m \quad (3.21)$$

$$\frac{\partial\psi_m}{\partial\rho_m} = \frac{\partial\psi_f}{\partial\rho_f} \quad \text{on } \Gamma_m \quad (3.22)$$

$$\rho_f\frac{\partial\psi_f}{\partial\rho_f} - \psi_f = P_\infty \quad \text{on } \Gamma_f. \quad (3.23)$$

Here, the tensor  $\hat{\mathbf{T}}$  is total stress in the swollen region and  $\mathbf{t} - \left(\rho_f\frac{\partial\psi_f}{\partial\rho_f} - \psi_f\right)\mathbf{n}_1$  is total traction on the boundary of swollen region.

In order to gain further insight into the nature of the resulting differential equations and the boundary conditions, we utilize the the definition of the “partial” pressures  $P_\alpha$  and chemical potential  $K_\alpha$  (where subscript  $\alpha$  is  $m$  for the swollen solid and  $f$  for the surrounding fluid) from Atkin and Craine [63, p. 225, 232]—keeping in mind that the Helmholtz potential per unit mass  $A_\alpha$  is given by  $\psi_\alpha/\rho_\alpha$ —to get

$$P_\alpha := \rho_\alpha^2 \frac{\partial A_\alpha}{\partial \rho_\alpha} = \rho_\alpha \frac{\partial \psi_\alpha}{\partial \rho_\alpha} - \psi_\alpha \quad (3.24)$$

$$K_\alpha := \frac{\partial(\rho_\alpha A)}{\partial \rho_\alpha} = \frac{\partial \psi_\alpha}{\partial \rho_\alpha} = \frac{P_\alpha + \psi_\alpha}{\rho_\alpha} \quad (\text{for } \alpha = m, f) \quad (3.25)$$

Then, in terms of the pressures and the chemical potentials, the differential equation

of system rewritten as

$$\operatorname{div}(\hat{\mathbf{T}}) = \mathbf{0} \quad \text{in } \Omega_m \quad (3.26)$$

$$\operatorname{grad}(K_m) = 0 \quad \text{in } \Omega_m \quad (3.27)$$

$$\operatorname{grad}(P_f) = 0 \quad \text{in } \Omega_f \quad (3.28)$$

while the natural boundary condition reduces to

$$\hat{\mathbf{T}}\mathbf{n}_1 = \mathbf{t} - P_f\mathbf{n}_1 \quad \text{on } \Gamma_m \quad (3.29)$$

$$K_m = K_f \quad \text{on } \Gamma_m \quad (3.30)$$

$$P_f = P_\infty \quad \text{on } \Gamma_f \quad (3.31)$$

Note that the differential equation (3.27) implies that the chemical potential in the swollen solid is constant, while the boundary condition (3.30) implies that the chemical potential is continuous across the interface  $\Gamma_m$ . This latter condition is the key result of our investigations of the equilibrium. As we shall see presently, the a-priori use of the volume additivity constraint as well as the incompressibility constraint will completely obscure the issue.

## 2. The volume additivity constraint as a limit of unconstrained body

Until now  $\psi_m$  has been assumed to be a function of  $\mathbf{F}$  and  $\rho_m$  and the volume additivity constraint as well as the incompressibility of the surrounding fluid have not been imposed. Rather than treat these two conditions as constraints, we shall approach it from the point of view of the limiting case when the compressibility of the fluid and the swollen polymer tend to zero. To this end, we use the auxiliary variable  $\phi$  (defined in (3.7)) and rewrite the constitutive equations for the Helmholtz

potential in the form

$$\psi_m = \hat{\psi}(\mathbf{F}, \rho_m) = \psi^*(\mathbf{F}, \phi) \quad (3.32)$$

Using chain rule, (3.25) and the first term of (3.26) reduce to

$$K_m = \frac{\partial \hat{\psi}}{\partial \rho_m} = \frac{\partial \psi^*}{\partial \phi} = \frac{P_m + \psi_m}{\rho_m} \quad (3.33)$$

$$\frac{\partial \hat{\psi}}{\partial \mathbf{F}} \mathbf{F}^T = \frac{\partial \psi^*}{\partial \mathbf{F}} \mathbf{F}^T + \frac{(\rho_{mo} - \rho_{fo})}{J} K_m \mathbf{I}, \quad (3.34)$$

and  $\hat{\mathbf{T}}$  results in

$$\hat{\mathbf{T}} = \frac{\partial \hat{\psi}}{\partial \mathbf{F}} \mathbf{F}^T - P_m \mathbf{I} = \frac{\partial \psi^*}{\partial \mathbf{F}} \mathbf{F}^T - ((\phi + \rho_{fo}) K_m - \psi^*) \mathbf{I}. \quad (3.35)$$

Now, in the limit when the fluid becomes incompressible, the bulk modulus (defined as the second derivative of the Helmholtz potential of the fluid with respect to the specific volume) becomes infinite in such a way the fluid pressure  $P_f$  defined in (3.24) remains finite and is no longer determined from a constitutive equation. Instead it is determined from the boundary value problem upon the use of the incompressibility constraint. From the definition of the pressure of fluid,  $P_f$  is the function of  $\rho_f$ , i.e.,

$$P_f = f(\rho_f) = \rho_f \frac{\partial \psi_f(\rho_f)}{\partial \rho_f} - \psi_f(\rho_f) \quad (3.36)$$

In the limiting case the variation of density  $\Delta \rho_f = \rho_f - \rho_{fo}$  go to zero, and expanding (3.36) as a Taylor series around  $\rho_f = \rho_{fo}$  gives

$$P_f = f(\rho_{fo}) + \frac{\partial f}{\partial \rho_f} \Big|_{\rho_f = \rho_{fo}} \Delta \rho_f + \dots \quad (3.37)$$

$f(\rho_{fo})$  is zero, because the reference density of the fluid corresponds to that in the stress free state. At the limit,  $\frac{\partial f}{\partial \rho_f} \Big|_{\rho_f = \rho_{fo}} \rightarrow \infty$  and  $\Delta \rho_f \rightarrow 0$  in such a way their product remains finite (See details in Ogden[74]). Then  $\rho_f$  becomes  $\rho_{fo}$ , and  $P_f$  becomes arbitrary but finite.

A similar argument using the volume additivity constraint (which reduces to  $\phi \rightarrow 0$ ), reveals the startling result that now the chemical potential  $K_m$  becomes finite and indeterminate and its value must now be determined by the solution of the boundary value problem. i.e.,  $K_m$  defined (3.25) can be expanded to a Taylor series around  $\phi = 0$  as

$$K_m(\phi) = \frac{\partial\psi^*}{\partial\phi}(0) + \frac{\partial^2\psi^*}{\partial\phi^2} |_{\phi=0} \phi + \dots \quad (3.38)$$

where  $\frac{\partial\psi^*}{\partial\phi}(0)$  is a finite value of chemical potential  $K_m(0)$  at  $\phi = 0$ . At the limit  $\frac{\partial^2\psi^*}{\partial\phi^2} |_{\phi=0} \rightarrow \infty$  and  $\phi \rightarrow 0$  in such a way their product remains finite. So the sum of the initial finite value of chemical potential and the finite value at the limit case yield an arbitral but finite value chemical potential. Also at the limit  $\phi$  becomes zero. Thus, when the various kinematical constraints are imposed through a limiting process, it follows from (3.26), (3.27), (3.28) and (3.35) that the equations of system are given by

$$\operatorname{div}\left(\frac{\partial\psi^*}{\partial\mathbf{F}}\mathbf{F}^T - (\rho_{fo}K_m - \psi^*)\mathbf{I}\right) = \mathbf{0} \quad \text{on } \Omega_m \quad (3.39)$$

$$\operatorname{grad}(K_m) = \mathbf{0} \quad \text{on } \Omega_m \quad (3.40)$$

$$\operatorname{grad}(P_f) = \mathbf{0} \quad \text{on } \Omega_f. \quad (3.41)$$

Boundary conditions (3.29),(3.30) and (3.31) become

$$\left(\frac{\partial\psi^*}{\partial\mathbf{F}}\mathbf{F}^T - (\rho_{fo}K_m - \psi^*)\mathbf{I}\right)\mathbf{n}_1 = \mathbf{t} - (\rho_{fo}K_f - \psi_f)\mathbf{n}_1 \quad \text{on } \Gamma_m \quad (3.42)$$

$$K_m = K_f \quad \text{on } \Gamma_m \quad (3.43)$$

$$P_f = P_\infty \quad \text{on } \Gamma_f. \quad (3.44)$$

We now see the source of the trouble in identifying the various terms when the volume additivity constraint is used a-priori. The role of the chemical potential becomes completely hidden and indeed can be completely eliminated from consideration.

To see this, we multiply (3.40) by  $\rho_{fo}$  and add (3.39) so that the differential equations become

$$\operatorname{div}\left(\frac{\partial\psi^*}{\partial\mathbf{F}}\mathbf{F}^T + \psi^*\mathbf{I}\right) = \mathbf{0} \quad \text{on } \Omega_m \quad (3.45)$$

$$\operatorname{grad}(P_f) = \mathbf{0} \quad \text{on } \Omega_f. \quad (3.46)$$

Multiplying (3.43) by  $\rho_{fo}$  and adding (3.42) gives the boundary conditions as

$$\left(\frac{\partial\psi^*}{\partial\mathbf{F}}\mathbf{F}^T + (\psi^* - \psi_f)\mathbf{I}\right)\mathbf{n}_1 = \mathbf{t} \quad \text{on } \Gamma_m \quad (3.47)$$

$$(P_f - P_\infty)\mathbf{n}_2 = \mathbf{0} \quad \text{on } \Gamma_f \quad (3.48)$$

The differential equations (3.45), (3.46) and boundary condition (3.47),(3.48), form the governing equations for the saturated state of the system that obeys volume additivity. For the particular case where the traction on the swollen polymer is a constant normal traction, i.e.  $\mathbf{t} = p\mathbf{n}$ , one possible solution is

$$\frac{\partial\psi^*}{\partial\mathbf{F}}\mathbf{F}^T + (\psi^* - \psi_f)\mathbf{I} = -p\mathbf{I} \quad \text{on } \Omega_m \quad (3.49)$$

$$P_f = P_\infty \quad \text{on } \Omega_f \quad (3.50)$$

Thus, due to the volume additivity constraint, the chemical potential plays no role in determining the equilibrium swelling of the polymer.

Once the equations are obtained by a limiting process, it can be verified (see appendix A) that carrying out the variational procedure and using the Lagrangian multiplier technique to impose the constraints a-priori results in the same equations as listed above, but the limiting procedure provides clear insight for the system.

### C. The limiting procedure applied to thermomechanical constraints

In previous sections, we find that the limiting procedure of the constraint for unconstrained body helps identifying physical meaning of the constraint response. Here, using this advantage of the limiting procedure, we further investigate three thermo-mechanical constraints (a deformation-temperature constraint, a deformation-energy constraint and a deformation-entropy constraint). These constraints are obtained as limits of unconstrained thermoelastic materials and we show that the deformation-energy constraint is equivalent to the deformation-entropy constraint. Also we shows that these constraints can be derived from appropriate Helmholtz potentials.

We model the thermoelastic response of a peroxide cured vulcanizate of natural rubber and show that imposing the constraint that the volume change depends only on the internal energy leads to very good prediction of the stress and temperature response under isothermal and isentropic deformations.

#### 1. Thermomechanical formulation for unconstrained thermoelasticity

In order to elucidate the precise nature of various constraints in thermoelasticity, we shall begin with various equivalent formulations of the constitutive equations for such variables. These formulations differ in the set of independent variables that are used in the constitutive theory.

Our first formulation will be based on the familiar Helmholtz potential. Here, the independent variables are the deformation gradient  $\mathbf{F}$  and the temperature  $\theta$ . The *equation of state*, from which the stress  $\mathbf{T}$  response and the entropy  $\eta$  are obtained, is given by

$$\psi = \hat{\psi}(\mathbf{F}, \theta). \quad (3.51)$$

where  $\psi$  is the specific Helmholtz potential. The general results of thermoelasticity

give the Cauchy stress  $\mathbf{T}$  and the entropy per unit mass  $\eta$  from the Helmholtz potential  $\psi$  by

$$\mathbf{T} = \rho \frac{\partial \hat{\psi}}{\partial \mathbf{F}} \mathbf{F}^T, \quad (3.52)$$

$$\eta = -\frac{\partial \hat{\psi}}{\partial \theta}. \quad (3.53)$$

where  $\rho$  is the current density. The entropy  $\eta$  is assumed to be a monotonically increasing function with respect to  $\theta$ . We will refer to (3.51–3.53) as the Helmholtz potential form of the equations of state or simply the  $\{\mathbf{F}, \theta\}$  formulation. The constitutive expression can be rewritten in the energetic form ( $\{\mathbf{F}, \eta\}$  formulation) using the Legendre transformation

$$\varepsilon = \psi - \theta \frac{\partial \psi}{\partial \theta} \quad (3.54)$$

Solving (3.53) for  $\theta$  in terms of  $\eta$  and  $\mathbf{F}$  and substituting the result into (3.54), we obtain

$$\varepsilon = \hat{\varepsilon}(\mathbf{F}, \eta) \quad (3.55)$$

where independent state variables are  $\mathbf{F}$  and  $\eta$ . Also, from  $\varepsilon$ , the stress and the absolute temperature are obtained as

$$\mathbf{T} = \rho \frac{\partial \hat{\varepsilon}}{\partial \mathbf{F}}, \quad (3.56)$$

$$\theta = \frac{\partial \hat{\varepsilon}}{\partial \eta} > 0. \quad (3.57)$$

Now (3.57) implies that (3.55) is invertible for  $\eta$  as a function of  $\mathbf{F}$  and  $\varepsilon$ , so that the constitutive expression can be rewritten in the entropic form ( $\{\mathbf{F}, \varepsilon\}$  formulation) and the equation of state reduces to

$$\eta = \hat{\eta}(\mathbf{F}, \varepsilon) \quad (3.58)$$



The Cauchy stress  $\mathbf{T}$  and the temperature  $\theta$  are defined by

$$\mathbf{T} = -\rho \left( \frac{\partial \hat{\eta}}{\partial \varepsilon} \right)^{-1} \frac{\partial \hat{\eta}}{\partial \mathbf{F}} \mathbf{F}^T \quad (3.59)$$

$$\theta = \left( \frac{\partial \hat{\eta}}{\partial \varepsilon} \right)^{-1} > 0 \quad (3.60)$$

(3.58–3.60) is referred as the entropic form of the equations of state or  $\{\mathbf{F}, \varepsilon\}$  formulation, where the independent variables are  $\mathbf{F}$  and  $\varepsilon$ .

In thermoelasticity, the positive definitions of certain material parameters obtained from the second derivatives of the potential function are considered as a mark of stability (see Scott [77]). It is generally assumed that the specific heat at constant deformation and the bulk modulus must be positive for stability (see Scott [77], Gunton and Saunders [78]). The specific heat at constant deformation  $C_v$  and the specific heat at constant stress  $C_p$  are defined by (see, e.g., Scott [79])

$$C_v = \theta \left( \frac{\partial \eta}{\partial \theta} \right)_{\text{fixed } \mathbf{F}}, \quad C_p = \theta \left( \frac{\partial \eta}{\partial \theta} \right)_{\text{fixed } \mathbf{T}} \quad (3.61)$$

and, through mathematical manipulation (see Callen [76, ch.7]),  $C_v$  is derived from constitutive expressions in the three different formulations as

$$C_v = -\theta \frac{\partial^2 \hat{\psi}}{\partial \theta^2} = \frac{\partial \hat{\varepsilon}}{\partial \eta} \left( \frac{\partial^2 \hat{\varepsilon}}{\partial \eta^2} \right)^{-1} = -\left( \frac{\partial \hat{\eta}}{\partial \varepsilon} \right)^2 \left( \frac{\partial^2 \hat{\eta}}{\partial \varepsilon^2} \right)^{-1}. \quad (3.62)$$

Using the Maxwell relation (also see Callen [76, ch.7] and Scott [79]), the bulk modulus at constant temperature  $K_\theta$  can be obtained as

$$\begin{aligned} K_\theta &= \rho_o \frac{\partial^2 \hat{\psi}}{\partial J^2} = \rho_o \frac{\partial^2 \hat{\varepsilon}}{\partial J^2} - \rho_o \left( \frac{\partial^2 \hat{\varepsilon}}{\partial J \partial \eta} \right)^2 \left( \frac{\partial^2 \hat{\varepsilon}}{\partial \eta^2} \right)^{-1} \\ &= -\rho_o \left( \frac{\partial \hat{\eta}}{\partial \varepsilon} \right)^{-1} \frac{\partial^2 \hat{\eta}}{\partial J^2} + \rho_o \left( \frac{\partial \hat{\eta}}{\partial \varepsilon} \right)^{-1} \left( \frac{\partial^2 \hat{\eta}}{\partial \varepsilon \partial J} \right)^2 \left( \frac{\partial^2 \hat{\eta}}{\partial \varepsilon^2} \right)^{-1}. \end{aligned} \quad (3.63)$$

The results in this section are tabulated in Table I for convenience.

Table I. Summary of constitutive relationships for unconstrained case

	$\{\mathbf{F}, \theta\}$ formulation	$\{\mathbf{F}, \eta\}$ formulation	$\{\mathbf{F}, \varepsilon\}$ formulation
Equation of state	$\psi = \hat{\psi}(\mathbf{F}, \theta)$	$\varepsilon = \hat{\varepsilon}(\mathbf{F}, \eta)$	$\eta = \hat{\eta}(\mathbf{F}, \varepsilon)$
Dependent variables	$\mathbf{T} = \rho \frac{\partial \hat{\psi}}{\partial \mathbf{F}} \mathbf{F}^T$ $\eta = -\frac{\partial \hat{\psi}}{\partial \theta}$	$\mathbf{T} = \rho \frac{\partial \hat{\varepsilon}}{\partial \mathbf{F}} \mathbf{F}^T$ $\theta = \frac{\partial \hat{\varepsilon}}{\partial \eta}$	$\mathbf{T} = -\rho \left(\frac{\partial \hat{\eta}}{\partial \varepsilon}\right)^{-1} \frac{\partial \hat{\eta}}{\partial \mathbf{F}} \mathbf{F}^T$ $\theta = \left(\frac{\partial \hat{\eta}}{\partial \varepsilon}\right)^{-1}$
Specific heat	$C_v = -\theta \frac{\partial^2 \psi}{\partial \theta^2}$	$C_v = \frac{\partial \varepsilon}{\partial \eta} \left(\frac{\partial^2 \varepsilon}{\partial \eta^2}\right)^{-1}$	$C_v = -\left(\frac{\partial \eta}{\partial \varepsilon}\right)^2 \left(\frac{\partial^2 \eta}{\partial \varepsilon^2}\right)^{-1}$

## 2. Thermoelasticity with constraints

In a general elastic material, it is clear that the entropy  $\eta$  given by (3.53) is a function of both deformation gradient and temperature. Many polymeric materials are characterized by the assumption that the entropy  $\eta$  is given by

$$\eta = \tilde{\eta}(\mathbf{F}). \quad (3.64)$$

Usually, in the  $\{\mathbf{F}, \theta\}$  formulation, this is treated as a constitutive assumption in the sense that (3.53) and (3.64) imply that  $\psi$  must be affine in  $\theta$ . However in the  $\{\mathbf{F}, \eta\}$  formulation, such as that used here and by Scott [80, 79],  $\mathbf{F}$  and  $\eta$  are the independent variables so that the equation (3.64) may be considered as a specific case of a general deformation-entropy constraint of the form

$$f(\mathbf{F}, \eta) = 0. \quad (3.65)$$

In other words, the relationship (3.64) can be viewed in two different ways i) as special constitutive assumption obtained from a Helmholtz potential in the classical  $\{\mathbf{F}, \theta\}$  formulation where  $\eta$  is a derived quantity, or ii) as a special case of an entropy-deformation constraint (3.65) in the  $\{\mathbf{F}, \eta\}$  formulation. In the former case, there is no need for the introduction of a constraint response whereas the same equation (3.64) would require a constraint response in the  $\{\mathbf{F}, \eta\}$  formulation. It is clear that the final differential equations must be the same, no matter which formulation is used. We shall explore this issue in more detail.

In order to investigate the effect of constraints in a thermoelastic body, we shall consider three classes of constraints (a) deformation-temperature constraints, (b) deformation-entropy constraints and (c) deformation-energy constraints. The different formulations of the basic constitutive relations are specifically suited to investigate specific classes of constraints.

a. Deformation-temperature constraint as a limit of an unconstrained body

We first consider the  $\{\mathbf{F}, \theta\}$  formulation and consider a constraint relating the deformation gradient and temperature in the form

$$\theta = T(\mathbf{F}), \tag{3.66}$$

Such a constraint was originally proposed as a generalization of a purely mechanical constraint such as incompressibility, to allow for thermal expansion but retain incompressibility under isothermal conditions. As Scott [80] in the context of thermoelasticity and Baek and Srinivasa [81] in the context of diffusion showed, rather than imposing the constraints directly via Lagrange multipliers, considering them as limiting cases helps to understand the behavior of the material and to provide a physical meaning to the constraint response.

Thus, consider an unconstrained thermoelastic material and introduce an auxiliary variable  $\phi$  as

$$\phi = \theta - T(\mathbf{F}) \quad (3.67)$$

Instead of augmenting the Helmholtz potential energy for the constrained material (for example Scott [79] used the form  $\psi^* = \psi + \frac{1}{2}\chi\phi^2$ ), we can choose  $\mathbf{F}$  and  $\phi$  as independent variables instead of  $\mathbf{F}$  and  $\theta$  for the Helmholtz potential function. Using (3.67), the equation of state (3.51) for an unconstrained material can be written in the form;

$$\psi = \hat{\psi}(\mathbf{F}, \theta) = \hat{\psi}(\mathbf{F}, \phi + T(\mathbf{F})) = \tilde{\psi}(\mathbf{F}, \phi). \quad (3.68)$$

Using the chain-rule, the entropy  $\eta$  becomes

$$\eta = -\frac{\partial\psi}{\partial\theta} = -\frac{\partial\tilde{\psi}}{\partial\phi} \quad (3.69)$$

and the Cauchy stress  $\mathbf{T}$  is given by

$$\mathbf{T} = \rho \frac{\partial\tilde{\psi}}{\partial\mathbf{F}} \mathbf{F}^T + \rho\eta \frac{\partial T}{\partial\mathbf{F}} \mathbf{F}^T. \quad (3.70)$$

We now consider the limit when  $\phi$  tends to zero. Expanding  $\eta$  as a Taylor series around  $\phi = 0$  as

$$\eta(\phi) = -\left(\frac{\partial\tilde{\psi}}{\partial\phi}\right)_{|\phi=0} - \left(\frac{\partial^2\tilde{\psi}}{\partial\phi^2}\right)_{|\phi=0} \phi - \dots \quad (3.71)$$

where  $\partial\tilde{\psi}/\partial\phi$  is a finite value at  $\phi = 0$ . In the limit, we assume that  $\partial^2\tilde{\psi}/\partial\phi^2|_{\phi=0} \rightarrow \pm\infty$  and  $\phi \rightarrow 0$  in such a way their product remains finite. It is also assumed that higher-order terms in (3.71) are successively of smaller orders of magnitude and give no contribution to  $\eta$  in the limit. So the sum of the terms in (3.71) yields an arbitrary but finite value for  $\eta$ . Thus in the limit, the entropy becomes an independent variable and plays the role of Lagrange multiplier whereas the temperature is given by (3.66), although for the unconstrained situation the temperature is the independent variable

and the entropy is a derived quantity. This limiting procedure also imply that in the limit as  $\phi \rightarrow 0$  the Helmholtz potential becomes a function of the deformation gradient  $\mathbf{F}$  alone, i.e.,

$$\lim_{\phi \rightarrow 0} \tilde{\psi}(\mathbf{F}, \phi) = \tilde{\psi}(\mathbf{F}, 0) = F(\mathbf{F}). \quad (3.72)$$

Thus, the stress reduces to

$$\mathbf{T} = \rho \frac{\partial F(\mathbf{F})}{\partial \mathbf{F}} \mathbf{F}^T + \rho \eta \frac{\partial T(\mathbf{F})}{\partial \mathbf{F}} \mathbf{F}^T. \quad (3.73)$$

As we mentioned before, the positiveness of  $C_v$  and  $K_\theta$  are desirable for the stability of the body and the sign of  $\partial^2 \tilde{\psi} / \partial \phi^2|_{\phi=0}$  is critical in deciding the sign of the second derivatives of the Helmholtz potential. First, let  $\partial^2 \tilde{\psi} / \partial \phi^2|_{\phi=0} \rightarrow -\infty$ . Then, the specific heat  $C_v$  defined by (3.62) becomes positive infinity in the limit, by expanding (3.62) as

$$C_v = -T(\mathbf{F}) \left( \frac{\partial^2 \tilde{\psi}}{\partial \phi^2} \right)_{|\phi=0} - T(\mathbf{F}) \left( \frac{\partial^3 \tilde{\psi}}{\partial \phi^3} \right)_{|\phi=0} \phi \dots \rightarrow \infty. \quad (3.74)$$

Using the chain-rule, the bulk modulus at the constant temperature  $K_\theta$  defined in (3.63) is expanded as

$$K_\theta = \rho_o \frac{\partial^2 \tilde{\psi}}{\partial J^2} = \rho_o \left\{ \frac{\partial^2 \tilde{\psi}}{\partial J^2} - 2 \frac{\partial^2 \tilde{\psi}}{\partial J \partial \phi} \frac{\partial T}{\partial J} - \frac{\partial \tilde{\psi}}{\partial \phi} \frac{\partial^2 T}{\partial J^2} + \frac{\partial^2 \tilde{\psi}}{\partial \phi^2} \left( \frac{\partial T}{\partial J} \right)^2 \right\}_{|\phi=0} + \dots \quad (3.75)$$

In the limit as  $\phi \rightarrow 0$  and  $\partial^2 \tilde{\psi} / \partial \phi^2|_{\phi=0} \rightarrow -\infty$ , assuming that the first derivative of  $\tilde{\psi}$  with respect to  $\phi$  and the derivatives of  $T$  in (3.75) are finite, the bulk modulus  $K_\theta$  goes negative infinity. Thus, the assumption  $\partial^2 \tilde{\psi} / \partial \phi^2|_{\phi=0} \rightarrow -\infty$  implies that the specific heat at constant deformation tends to  $+\infty$  but isothermal bulk modulus tends to  $-\infty$ , which implies loss of stability of the body.

Next, if we assume that  $\partial^2 \tilde{\psi} / \partial \phi^2|_{\phi=0} \rightarrow \infty$  at the limit as  $\phi \rightarrow 0$ , the isothermal bulk modulus goes to positive infinity, but the specific heat at constant deforma-

tion becomes negative infinity. This again physically unacceptable. It is also shown by Scott [79] that, assuming an augmented form of the Helmholtz potential and a deformation-temperature constraint in which the temperature is a linear function of the deformation gradient, the specific heat becomes negative in the limit and this corresponds to loss of stability. Thus the limiting process reveals that, although the deformation temperature constraint appears to be a straight forward generalization of the incompressibility constraint, it results in the material becoming unstable.

It is instructive to note that the same constitutive equations may be obtained without the use of a limiting process in the  $\{\mathbf{F}, \eta\}$  formulation. In this case the condition (3.66) can be simply inferred by using the constitutive form

$$\varepsilon = \hat{\varepsilon}(\mathbf{F}, \eta) = F(\mathbf{F}) + \eta T(\mathbf{F}). \quad (3.76)$$

Using (3.57), the energy function (3.76) immediately gives (3.66). Furthermore, we get

$$\mathbf{T} = \rho \frac{\partial F(\mathbf{F})}{\partial \mathbf{F}} \mathbf{F}^T + \rho \eta \frac{\partial T(\mathbf{F})}{\partial \mathbf{F}} \mathbf{F}^T. \quad (3.77)$$

Of course, in this latter formulation, the limiting process is not used so that the sign of the unstable response is not evident.

#### b. Deformation-entropy constraint as a limit of an unconstrained body

We consider the  $\{\mathbf{F}, \eta\}$  formulation and a different generalization of the purely mechanical constraint in the form

$$f(\mathbf{F}, \eta) = 0. \quad (3.78)$$

Under the assumption that  $f$  is monotonically increasing function for  $\eta$ , i.e.,

$$\frac{\partial f}{\partial \eta} > 0, \quad (3.79)$$

the constraint can be rewritten in the form

$$\eta = S(\mathbf{F}). \quad (3.80)$$

Scott [80] has introduced a linearized form of (3.80) connecting the deformation and the entropy as an alternative to the temperature-deformation constraint (3.66).

In this case the variable  $\phi$  introduced in (3.67) is replaced by

$$\phi = \eta - S(\mathbf{F}). \quad (3.81)$$

Using (3.81), the constitutive equation (3.55) for the internal energy of an unconstrained material can be rewritten in the form

$$\varepsilon = \hat{\varepsilon}(\mathbf{F}, \eta) = \tilde{\varepsilon}(\mathbf{F}, \phi). \quad (3.82)$$

Using the chain-rule, it can be shown that  $\partial\tilde{\varepsilon}/\partial\phi$  is the absolute temperature, i.e.,

$$\theta = \frac{\partial\varepsilon}{\partial\eta} = \frac{\partial\tilde{\varepsilon}}{\partial\phi}, \quad (3.83)$$

and the Cauchy stress  $\mathbf{T}$  now becomes

$$\mathbf{T} = \rho \frac{\partial\tilde{\varepsilon}}{\partial\mathbf{F}} \mathbf{F}^T - \rho \theta \frac{\partial S}{\partial\mathbf{F}} \mathbf{F}^T. \quad (3.84)$$

We assume that, in the limit as  $\phi \rightarrow 0$ ,  $(\partial\tilde{\varepsilon}/\partial\phi)|_{\phi=0}$  is a finite value, and the product of  $\partial^2\tilde{\varepsilon}/\partial\phi^2|_{\phi=0} \rightarrow \infty$  and  $\phi$  is arbitrary and finite. Under these conditions, the function  $\theta$  in (3.83) can be expanded as a Taylor series around  $\phi = 0$  as

$$\theta(\phi) = \frac{\partial\tilde{\varepsilon}}{\partial\phi}|_{\phi=0} + \frac{\partial^2\tilde{\varepsilon}}{\partial\phi^2}|_{\phi=0}\phi + \dots \quad (3.85)$$

Higher-order terms in (3.85) are smaller orders of magnitude so that the sum of the

terms in (3.85) yields an arbitrary but finite value. In the limit, (3.82) reduces to

$$\lim_{\phi \rightarrow 0} \tilde{\varepsilon}(\mathbf{F}, \phi) = U(\mathbf{F}). \quad (3.86)$$

Thus, the constraint  $\eta = S(\mathbf{F})$  implies  $\varepsilon = U(\mathbf{F})$  and the stress is rewritten as

$$\mathbf{T} = \rho \frac{\partial U(\mathbf{F})}{\partial \mathbf{F}} \mathbf{F}^T - \rho \theta \frac{\partial S(\mathbf{F})}{\partial \mathbf{F}} \mathbf{F}^T. \quad (3.87)$$

We observe from (3.87) that the stress response is linear with respect to the temperature  $\theta$ .

From the conditions for the limit as  $\phi \rightarrow 0$  and  $\partial^2 \tilde{\varepsilon} / \partial \phi^2 |_{\phi=0} \rightarrow \pm \infty$ , the specific heat  $C_v$  goes to zero by expanding (3.62) as a Taylor series around  $\phi = 0$  as

$$C_v = \frac{\partial \tilde{\varepsilon}}{\partial \phi} \left( \frac{\partial^2 \tilde{\varepsilon}}{\partial \phi^2} \right)^{-1} + \left( 1 - \frac{\partial \tilde{\varepsilon}}{\partial \phi} \frac{\partial^3 \tilde{\varepsilon}}{\partial \phi^3} \left( \frac{\partial^2 \tilde{\varepsilon}}{\partial \phi^2} \right)^{-2} \right) \Big|_{\phi=0} \phi + \dots \rightarrow 0. \quad (3.88)$$

Using the chain-rule, the bulk modulus at constant temperature  $K_\theta$  given in (3.63) can be rewritten as

$$\begin{aligned} K_\theta &= \rho_o \left( \frac{\partial^2 \tilde{\varepsilon}}{\partial J^2} - 2 \frac{\partial^2 \tilde{\varepsilon}}{\partial J \partial \phi} \frac{\partial S}{\partial J} - \frac{\partial \tilde{\varepsilon}}{\partial \phi} \frac{\partial^2 S}{\partial J^2} + \frac{\partial^2 \tilde{\varepsilon}}{\partial \phi^2} \left( \frac{\partial S}{\partial J} \right)^2 \right) \\ &\quad - \rho_o \left( \frac{\partial^2 \tilde{\varepsilon}}{\partial \phi \partial J} - \frac{\partial^2 \tilde{\varepsilon}}{\partial \phi^2} \frac{\partial S}{\partial J} \right)^2 \left( \frac{\partial^2 \tilde{\varepsilon}}{\partial \phi^2} \right) \\ &= \rho_o \left\{ \frac{\partial^2 \tilde{\varepsilon}}{\partial J^2} - \frac{\partial \tilde{\varepsilon}}{\partial \phi} \frac{\partial^2 S}{\partial J^2} - \left( \frac{\partial \tilde{\varepsilon}}{\partial \phi \partial J} \right)^2 \left( \frac{\partial^2 \tilde{\varepsilon}}{\partial \phi^2} \right)^{-1} \right\} \end{aligned} \quad (3.89)$$

In the limit as  $\phi \rightarrow 0$ , the value of  $\partial^2 \tilde{\varepsilon} / \partial \phi^2 |_{\phi=0}$  goes to  $\pm \infty$  so that the last term of the right hand side of (3.89) vanishes. Finally, in the limit,  $K_\theta$  is reduced to

$$K_\theta = \rho_o \left( \frac{\partial^2 \tilde{\varepsilon}}{\partial J^2} - \theta \frac{\partial^2 S}{\partial J^2} \right) \Big|_{\phi=0} + \dots, \quad (3.90)$$

where  $\theta$  is arbitrary and finite. Thus, in the limit as  $\phi \rightarrow 0$  and  $\partial^2 \tilde{\varepsilon} / \partial \phi^2 |_{\phi=0} \rightarrow \pm \infty$ ,



$C_v$  goes to zero and the condition for the positive  $K_\theta$  becomes

$$\frac{\partial^2 \tilde{\varepsilon}}{\partial J^2} - \theta \frac{\partial^2 S}{\partial J^2} > 0. \quad (3.91)$$

Similar to the case of the deformation-temperature constraint, the equation (3.80), which is given as the deformation-entropy constraint in  $\{\mathbf{F}, \eta\}$  formulation, can be obtained as a constitutive relation derived from the Helmholtz potential form of the equation of state of the form

$$\psi(\mathbf{F}, \theta) = U(\mathbf{F}) - \theta S(\mathbf{F}). \quad (3.92)$$

Substituting (3.92) into (3.52), the stress  $\mathbf{T}$  derived as

$$\mathbf{T} = \rho \frac{\partial U(\mathbf{F})}{\partial \mathbf{F}} \mathbf{F}^T - \rho \theta \frac{\partial S(\mathbf{F})}{\partial \mathbf{F}} \mathbf{F}^T. \quad (3.93)$$

which results the same as (3.87). Also, substituting (3.92) into (3.62)<sub>1</sub> and (3.63)<sub>1</sub>, the specific heat  $C_v$  and the bulk modulus  $K_\theta$  derived as

$$C_v = 0 \quad (3.94)$$

$$K_\theta = \rho_o \frac{\partial^2 U}{\partial J^2} - \rho_o \theta \frac{\partial^2 S}{\partial J^2} \quad (3.95)$$

In this formulation, the temperature is independent variable.

### c. Deformation-energy constraint as a limit of an unconstrained body

In the section 3.2, the deformation-entropy constraint implies that the internal energy is a function of the deformation gradient only. Now, let us consider the deformation-energy constraint in the  $\{\mathbf{F}, \varepsilon\}$  formulation in the form

$$\varepsilon = U(\mathbf{F}). \quad (3.96)$$

Then, the auxiliary variable  $\phi$  is written as

$$\phi = \varepsilon - U(\mathbf{F}) \quad (3.97)$$

and  $\phi$  goes to zero where (3.96) hold. Using (3.97), the equation of state (3.58) of an unconstrained material can be written in the form;

$$\eta = \eta(\mathbf{F}, \varepsilon) = \tilde{\eta}(\mathbf{F}, \phi). \quad (3.98)$$

Using (3.59) and the chain-rule, the Cauchy stress  $\mathbf{T}$  becomes

$$\mathbf{T} = -\rho \left( \frac{\partial \tilde{\eta}}{\partial \phi} \right)^{-1} \left( \frac{\partial \tilde{\eta}}{\partial \mathbf{F}} \mathbf{F}^T - \frac{\partial \tilde{\eta}}{\partial \phi} \frac{\partial U}{\partial \mathbf{F}} \mathbf{F}^T \right) = \rho \frac{\partial U}{\partial \mathbf{F}} \mathbf{F}^T - \rho \left( \frac{\partial \tilde{\eta}}{\partial \phi} \right)^{-1} \frac{\partial \tilde{\eta}}{\partial \mathbf{F}} \mathbf{F}^T. \quad (3.99)$$

We also see that

$$\theta = \left( \frac{\partial \eta}{\partial \varepsilon} \right)^{-1} = \left( \frac{\partial \tilde{\eta}}{\partial \phi} \right)^{-1}. \quad (3.100)$$

Now we assume that  $(\partial \tilde{\eta} / \partial \phi)^{-1}|_{\phi=0}$  is a finite value and  $\partial^2 \tilde{\eta} / \partial \phi^2|_{\phi=0} \rightarrow \infty$  so that the product of  $\partial^2 \tilde{\eta} / \partial \phi^2$  and  $\phi$  becomes arbitrary and finite at the limit. Under these conditions  $\theta$  can be expanded as a Taylor series around  $\phi = 0$  as

$$\theta(\phi) = \left( \frac{\partial \tilde{\eta}}{\partial \phi} \right)^{-1}_{|\phi=0} - \frac{\partial^2 \tilde{\eta}}{\partial \phi^2} \left( \frac{\partial \tilde{\eta}}{\partial \phi} \right)^{-2}_{|\phi=0} \phi + \dots \quad (3.101)$$

where higher-order terms in (3.101) are smaller orders on magnitude. So the sum of the terms in (3.101) yields an arbitrary but finite value.

At the limit, the function of entropy becomes a function of  $\mathbf{F}$  alone,

$$\lim_{\phi \rightarrow 0} \tilde{\eta}(\mathbf{F}, \phi) = S(\mathbf{F}). \quad (3.102)$$

Substituting (3.102) into (3.99), the stress  $\mathbf{T}$  reduces to

$$\mathbf{T} = \rho \frac{\partial U(\mathbf{F})}{\partial \mathbf{F}} \mathbf{F}^T - \rho \theta \frac{\partial S(\mathbf{F})}{\partial \mathbf{F}} \mathbf{F}^T. \quad (3.103)$$

From the conditions for the limit as  $\phi \rightarrow 0$  and  $\partial^2 \tilde{\eta} / \partial \phi^2 \rightarrow -\infty$ , the specific heat  $C_v$  goes to zero by expanding (3.62) as a Taylor series around  $\phi = 0$  as

$$C_v = -\left(\frac{\partial \tilde{\eta}}{\partial \phi}\right)^2 \left(\frac{\partial^2 \tilde{\eta}}{\partial \phi^2}\right)^{-1} - \left(2\frac{\partial \tilde{\eta}}{\partial \phi} \left(\frac{\partial^2 \tilde{\eta}}{\partial \phi^2}\right)^{-1} - \frac{\partial^3 \tilde{\eta}}{\partial \phi^3} \left(\frac{\partial \tilde{\eta}}{\partial \phi}\right)^2 \left(\frac{\partial^2 \tilde{\eta}}{\partial \phi^2}\right)^{-2}\right)_{|\phi=0} \phi - \dots \rightarrow 0 \quad (3.104)$$

Using the chain-rule,  $K_\theta$  in (3.63) can be rewritten as

$$\begin{aligned} K_\theta &= -\rho_o \left(\frac{\partial \tilde{\eta}}{\partial \phi}\right)^{-1} \left(\frac{\partial^2 \tilde{\eta}}{\partial J^2} - 2\frac{\partial^2 \tilde{\eta}}{\partial J \partial \phi} \frac{\partial U}{\partial J} - \frac{\partial \tilde{\eta}}{\partial \phi} \frac{\partial^2 U}{\partial J^2} + \frac{\partial^2 \tilde{\eta}}{\partial \phi^2} \left(\frac{\partial U}{\partial J}\right)^2\right) \\ &\quad + \rho_o \left(\frac{\partial \tilde{\eta}}{\partial \phi}\right)^{-1} \left(\frac{\partial^2 \tilde{\eta}}{\partial \phi \partial J} - \frac{\partial^2 \tilde{\eta}}{\partial \phi^2} \frac{\partial U}{\partial J}\right)^2 \left(\frac{\partial^2 \tilde{\eta}}{\partial \phi^2}\right)^{-1} \\ &= -\rho_o \left(\frac{\partial \tilde{\eta}}{\partial \phi}\right)^{-1} \left\{ \frac{\partial^2 \tilde{\eta}}{\partial J^2} - \frac{\partial \tilde{\eta}}{\partial \phi} \frac{\partial^2 U}{\partial J^2} - \left(\frac{\partial^2 \tilde{\eta}}{\partial \phi \partial J}\right)^2 \left(\frac{\partial^2 \tilde{\eta}}{\partial \phi^2}\right)^{-1} \right\} \end{aligned} \quad (3.105)$$

In the limit as  $\phi \rightarrow 0$ , the value of  $\partial^2 \tilde{\eta} / \partial \phi^2|_{\phi=0}$  goes to  $\pm\infty$  so that the last term of the right hand side of (3.105) vanishes. Finally, in the limit,  $K_\theta$  is reduced to

$$K_\theta = \rho_o \left(\frac{\partial^2 U}{\partial J^2} - \theta \frac{\partial^2 \tilde{\eta}}{\partial J^2}\right)_{|\phi=0} + \dots, \quad (3.106)$$

where  $\theta$  is arbitrary and finite. Thus, in the limit as  $\phi \rightarrow 0$  and  $\partial^2 \tilde{\eta} / \partial \phi^2|_{\phi=0} \rightarrow \pm\infty$ ,  $C_v$  goes to zero and the condition for the positive  $K_\theta$  becomes

$$\frac{\partial^2 U}{\partial J^2} - \theta \frac{\partial^2 \tilde{\eta}}{\partial J^2} > 0. \quad (3.107)$$

From the section 3.2 and 3.3, the deformation-entropy constraint,  $\eta = S(\mathbf{F})$ , implies that the constitutive form for the internal energy is a function of deformation alone, i.e.,  $\eta = S(\mathbf{F}) \rightarrow \varepsilon = U(\mathbf{F})$ , and the deformation-energy constraint  $\varepsilon = U(\mathbf{F})$  implies that the entropy is a function of the deformation gradient alone, i.e.,

$$\eta = S(\mathbf{F}) \iff \varepsilon = U(\mathbf{F}). \quad (3.108)$$

It is also shown that the explicit form of constraints of both entropy-displacement and

energy-displacement implies the same form of stress and temperature to be arbitrary and finite. So, the Helmholtz potential function in  $\{\mathbf{F}, \theta\}$  formulation introduced in (3.92) includes not only (3.80) but also (3.96) as constitutive equations. That is, the equation (3.80) and (3.96) are delivered as constitutive equations from the Helmholtz potential of the form

$$\psi(\mathbf{F}, \theta) = U(\mathbf{F}) - \theta S(\mathbf{F}). \quad (3.109)$$

The stress response derived from (3.109) is identical to (3.103) and the specific heat turns out to be zero.

As Scott [79] found, if we set  $C_v = 0$  in the constitutive equation, we can obtain the same constitutive response as those from the deformation-entropy and deformation-energy constraints. To see this, substituting  $C_v = 0$  into (3.61), we obtain

$$\left(\frac{\partial \eta}{\partial \theta}\right)_{\text{fixed } \mathbf{F}} = 0, \quad (3.110)$$

which implies the entropy is a function of  $\mathbf{F}$  only. Also substituting  $C_v = 0$  into (3.62) results in

$$\frac{\partial^2 \hat{\psi}}{\partial \theta^2} = 0, \quad (3.111)$$

which implies the Helmholtz potential is linear with respect to the temperature. Thus, simply setting  $C_v = 0$  in the Helmholtz potential is equivalent to the deformation-entropy and deformation-energy constraints.

Therefore the following four assumption are equivalent:

1.  $\eta = S(\mathbf{F})$
2.  $\varepsilon = U(\mathbf{F})$
3.  $\psi = U(\mathbf{F}) - \theta S(\mathbf{F})$
4.  $C_v = 0$ .

Table II. Thermomechanical constraints and equivalent forms of potential energy functions

Constraint form	$\varepsilon = U(\mathbf{F})$ $\eta = S(\mathbf{F})$	$\theta = T(\mathbf{F})$ $\psi = F(\mathbf{F})$
Equivalent form	$\psi(\mathbf{F}, \theta) = U(\mathbf{F}) - \theta S(\mathbf{F})$	$\varepsilon(\mathbf{F}, \eta) = F(\mathbf{F}) + \eta T(\mathbf{F})$
Stress	$\mathbf{T} = \rho \frac{\partial U}{\partial \mathbf{F}} \mathbf{F}^T - \rho \theta \frac{\partial S}{\partial \mathbf{F}} \mathbf{F}^T$ $\theta$ independent	$\mathbf{T} = \rho \frac{\partial F}{\partial \mathbf{F}} \mathbf{F}^T + \rho \eta \frac{\partial T}{\partial \mathbf{F}} \mathbf{F}^T$ $\eta$ independent
Specific heat	$C_v = 0$	$C_v = \infty$
Bulk modulus	$K_\theta = \rho_o \frac{\partial^2 U}{\partial J^2} - \rho_o \theta \frac{\partial^2 S}{\partial J^2}$	$K_\theta = -\infty$

We summarize the thermomechanical constraints and the equivalent forms of potential energy functions in Table II.

### 3. The application of thermomechanical constraint to a rubberlike material

In polymeric material, statistical mechanics considerations reveal that the entropy is significantly affected by isochoric deformation whereas the internal energy is hardly changed, so much so that a simple incompressible model assumes that (1) the material is incompressible (2)  $\eta = \hat{\eta}(\mathbf{F})$ , and (3) the energy is constant.

It has been shown that such idealization is inadequate for the realistic modeling of thermoelastic processes. Motivated by the results of the section 2, we consider a generalization of the above questions by assuming (a) The material is compressible and (b) the energy  $\varepsilon$  is a function of  $J$  alone. Note that the assumption (b) implies that, for isochoric deformations, the energy is constant in keeping the idealizations used in purely entropic elasticity. In view of the results presented in section 2, the

assumption (b) precludes the entropy  $\eta$  from being a function of the temperature, so that

$$\eta = S(\mathbf{F}). \quad (3.112)$$

Furthermore, the assumption on energy implies that the Helmholtz potential is of the form

$$\psi = -\theta S(\mathbf{F}) + \varepsilon(J). \quad (3.113)$$

A specific form for  $S(\mathbf{F})$  and  $\varepsilon(J)$  can be derived from the constitutive equation which was suggested by Chadwick [82] and result in quantitative agreement with experiments, by letting the specific heat  $C_v \rightarrow 0$ . To elaborate, Chadwick considered a Helmholtz potential of the form

$$\psi(\mathbf{F}, \theta) = \frac{\theta}{\theta_o} \left[ \psi_o(\mathbf{F}) - \varepsilon_o(\mathbf{F}) \right] + \varepsilon_o(\mathbf{F}) - A \left( \theta \ln \frac{\theta}{\theta_o} - \theta + \theta_o \right) \quad (3.114)$$

The stress  $\mathbf{T}$ , obtained by combining (3.52) and (3.114), is given by

$$\mathbf{T} = \rho \frac{\theta}{\theta_o} \frac{\partial \psi_o}{\partial \mathbf{F}} \mathbf{F}^T + \rho_o \left( 1 - \frac{\theta}{\theta_o} \right) \frac{\partial \varepsilon_o}{\partial J} \mathbf{I}. \quad (3.115)$$

and  $\eta$  is given by

$$\eta(\mathbf{F}, \theta) = -\frac{1}{\theta_o} \left[ \psi_o(\mathbf{F}) - \varepsilon_o(J) \right] + A \ln \frac{\theta}{\theta_o}. \quad (3.116)$$

The entropy  $\eta$  is separated into two parts: the first part is a function of the deformation gradient and the second part is a function of the temperature alone. The specific heat at constant deformation  $C_v$  and  $C_p$  at constant stress  $\mathbf{T} = \mathbf{T}^*$  are given by

$$C_v = A \quad (3.117)$$

$$C_p = C_v + \theta \frac{\partial \eta}{\partial J} \left( \frac{\partial J}{\partial \theta} \right)_{\mathbf{T}=\mathbf{T}^*} \quad (3.118)$$

We also note that value of  $C_v$  has no effect on the stress response.

In view of section 3, the equivalent form of Helmholtz potential for the deformation-

energy constraint can be obtained by setting  $C_v = 0$ . Thus, letting  $C_v \rightarrow 0$ , the Helmholtz potential reduces to

$$\psi(\mathbf{F}, \theta) = \frac{\theta}{\theta_o} \left[ \psi_o(\mathbf{F}) - \varepsilon_o(J) \right] + \varepsilon_o(J) \quad (3.119)$$

Comparing (3.119) with (3.113), the equivalent constraints are obtained as

$$\varepsilon = U(\mathbf{F}) = \varepsilon_o(J) \quad (3.120)$$

and

$$\eta = S(\mathbf{F}) = -\frac{1}{\theta_o} \left[ \psi_o(\mathbf{F}) - \varepsilon_o(J) \right]. \quad (3.121)$$

Using (3.103), the stress is obtained as

$$\mathbf{T} = \rho \frac{\theta}{\theta_o} \frac{\partial \psi_o}{\partial \mathbf{F}} \mathbf{F}^T + \rho_o \left( 1 - \frac{\theta}{\theta_o} \right) \frac{\partial \varepsilon_o}{\partial J} \mathbf{I} \quad (3.122)$$

which is the same as the stress of (3.115) in the unconstrained case.  $C_p$  is given by

$$C_p = \theta \frac{\partial \eta}{\partial J} \left( \frac{\partial J}{\partial \theta} \right)_{\mathbf{T}=\mathbf{T}^*} \quad (3.123)$$

For the application, we consider empirical functions used by Chadwick [82] (also see references therein) of the form

$$\psi_o(\mathbf{F}) = \frac{\mu}{\rho_o} (I_1 - 3J^{2/3}) + \frac{\kappa}{\rho_o m} \left( J + \frac{1}{m-1} J^{-m+1} - \frac{m}{m-1} \right) \quad (3.124)$$

$$\varepsilon_o(\mathbf{F}) = \frac{\kappa \alpha \theta_o}{\rho_o n} (J^n - 1). \quad (3.125)$$

We use thermoelastic material parameters of a peroxide-cured vulcanizate of natural rubber (see Chadwick [82] and Wood and Martin [83]) and they are the density  $\rho_o = 906.5 \text{ kg/m}^3$ , the shear modulus  $\mu = 4.2 \times 10^2 \text{ kPa}$ , the isothermal bulk modulus  $\kappa = 1.95 \times 10^6 \text{ kPa}$ , the volume coefficient of thermal expansion  $\alpha = 6.36 \times 10^{-4} \text{ K}^{-1}$ , the material constants  $m = 9$ , and  $n = 5/2$ . The initial temperature  $\theta_o$  is  $25^\circ\text{C}$ .

In order to compare the numerical results of the constrained case with those of the unconstrained case, we consider a simple homogeneous deformation of the form

$$x = J^{\frac{1}{3}}\lambda X \quad (3.126)$$

$$y = \frac{J^{\frac{1}{3}}}{\sqrt{\lambda}}Y \quad (3.127)$$

$$z = \frac{J^{\frac{1}{3}}}{\sqrt{\lambda}}Z. \quad (3.128)$$

where  $(X, Y, Z)$  are the position in reference configuration and  $(x, y, z)$  are the position in current configuration in Cartesian coordinate.  $\lambda$  is the isochoric biaxial stretch. The deformation gradient is calculated to

$$\mathbf{F} = J^{\frac{1}{3}} \begin{bmatrix} \lambda & 0 & 0 \\ 0 & \frac{1}{\sqrt{\lambda}} & 0 \\ 0 & 0 & \frac{1}{\sqrt{\lambda}} \end{bmatrix}, \quad \mathbf{B} = J^{\frac{2}{3}} \begin{bmatrix} \lambda^2 & 0 & 0 \\ 0 & \frac{1}{\lambda} & 0 \\ 0 & 0 & \frac{1}{\lambda} \end{bmatrix} \quad (3.129)$$

The invariants of  $\mathbf{B}$  are given by

$$I_1 = J^{2/3}(\lambda^2 + 2/\lambda), \quad I_2 = 2J^{4/3}\lambda, \quad I_3 = J^2. \quad (3.130)$$

Substituting (3.124) and (3.125) into (3.121), the deformation-entropy relation is obtained by

$$\eta = -\frac{\kappa}{\rho_o\theta_o} \left[ \frac{\mu}{\kappa}(I_1 - 3J^{2/3}) + \frac{J}{m} + \frac{J^{-m+1} - m}{m(m-1)} - \frac{\alpha\theta_o}{n}(J^n - 1) \right] \quad (3.131)$$

It follows from (3.122) that the stress  $\mathbf{T}$  is given by

$$\mathbf{T} = \frac{2\mu\theta}{J\theta_o} \left( \mathbf{B} - J^{\frac{2}{3}}\mathbf{I} \right) + \frac{\kappa\theta}{m\theta_o} \left( 1 - J^{-m} \right) \mathbf{I} + \kappa\alpha\theta_o J^{n-1} \left( 1 - \frac{\theta}{\theta_o} \right) \mathbf{I} \quad (3.132)$$

The volume-pressure relation for pure volume expansion can be found by substituting



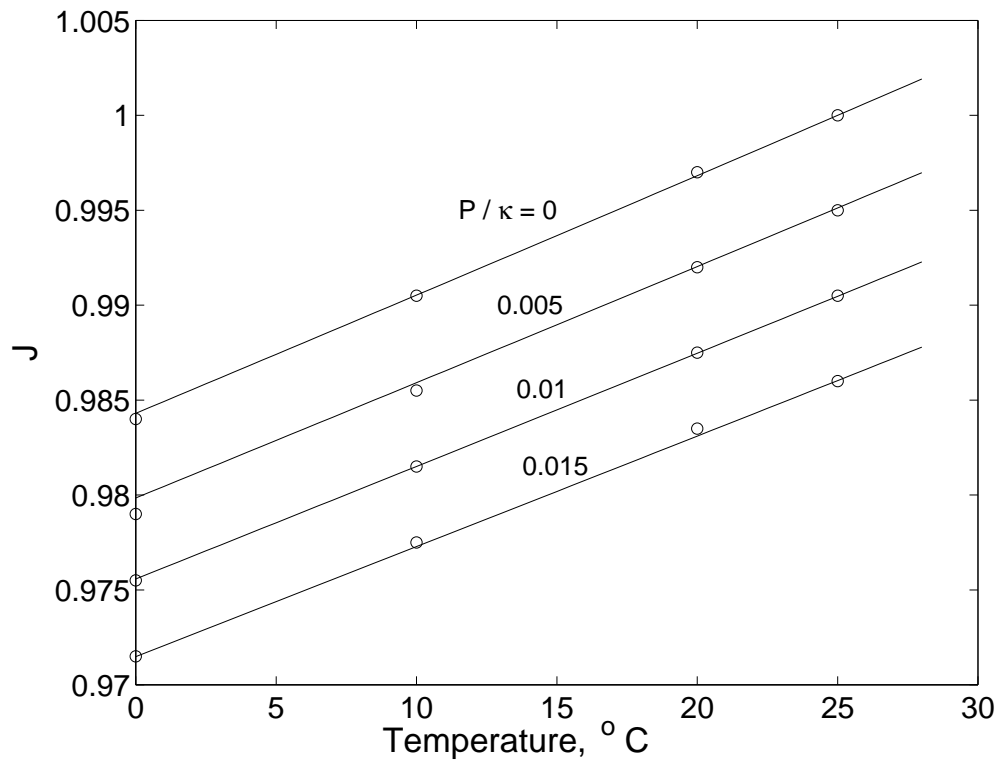


Fig. 7. Volume expansion with temperature variation for different ambient pressures. Experimental data is from Wood and Martin [83]

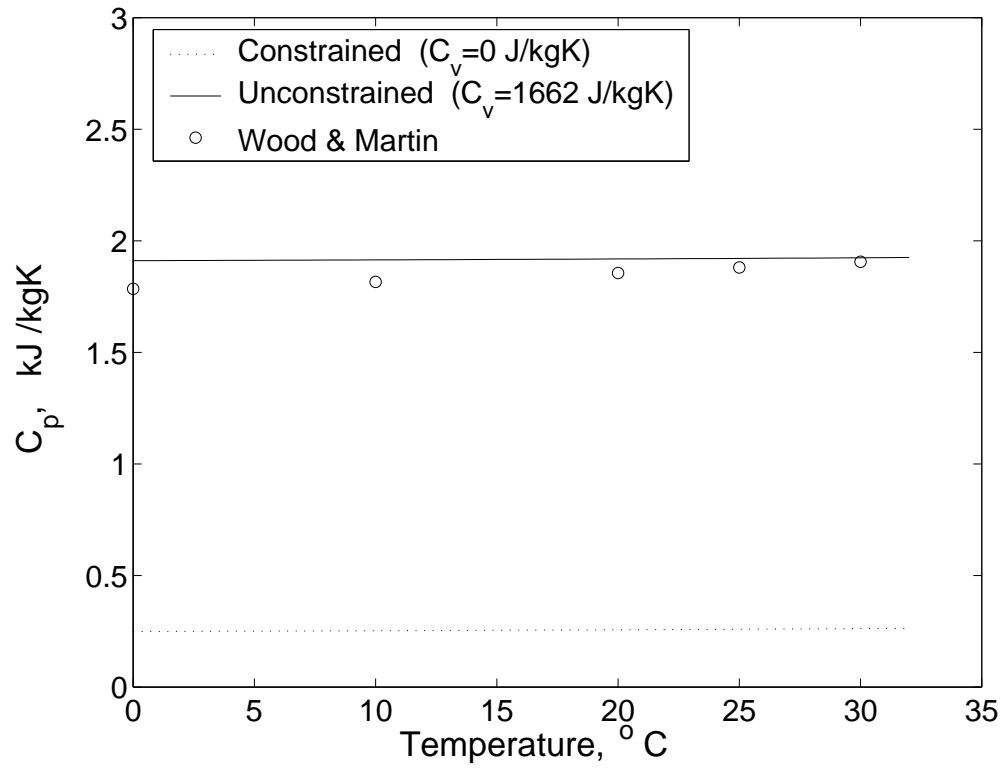


Fig. 8. Comparison  $C_p$  for  $C_v = 1.662$  kJ/kgK,  $C_p = 0$  kJ/kgK and data from Wood and Martin [83]

$\lambda = 1$  and  $\mathbf{T} = -P\mathbf{I}$  into (3.132), to give

$$-P = \frac{\kappa\theta}{m\theta_o}(1 - J^{-m}) + \kappa\alpha\theta_o J^{n-1}\left(1 - \frac{\theta}{\theta_o}\right) \quad (3.133)$$

Figure 7 shows the volume change-temperature curve for four different nondimensionalized pressures  $P/\kappa$ . From (3.133), the relation between temperature and volume change in isothermal process and at the stress free state is obtained by

$$\theta = \frac{-\kappa\alpha\theta_o J^{n-1}}{\frac{\kappa}{m\theta_o}(1 - J^{-m}) - \kappa\alpha J^{n-1}} \quad (3.134)$$

The specific heat at constant pressure  $C_p$  can be obtained from (3.123) and (3.132) for fixed value of the stress  $\mathbf{T}$  and  $\lambda$ . When  $\mathbf{T} = 0$  and  $\lambda = 1$ ,  $\partial J/\partial\theta|_{\mathbf{T}=0}$  can be obtain from (3.134) and substituting the result into (3.123) gives  $C_p$ -temperature curve shown in Figure 8. The results are compared with the unconstrained case and the experimental data of Wood and Martin [83].

Since the stress response in isothermal deformation is the same for both constrained and unconstrained cases, the difference between them in stress and temperature response has to be found in isentropic deformation. In order to find temperature and stress response in isentropic homogeneous extention for the constrained case, we substitute the value of  $\lambda$  and  $\eta = 0$  into (3.131) and obtain  $J$ . Then, the temperature and the biaxial stress are obtained from (3.132) by assuming other stress component to be zero except the axial stress  $T_{xx}$  which is set to be  $\sigma$ . The variation of temperature with respect to the axial stretch  $\Lambda$  for the isentropic process is plotted in Figure 9 where the axial stretch is defined by (see James and Guth [84])

$$\Lambda = \lambda(J/J_o)^{\frac{1}{3}}. \quad (3.135)$$

The non-dimensionalized temperature changes by 1% from the data when the axial stretch is doubled, and the absolute value of temperature changes by about  $3^\circ C$ .

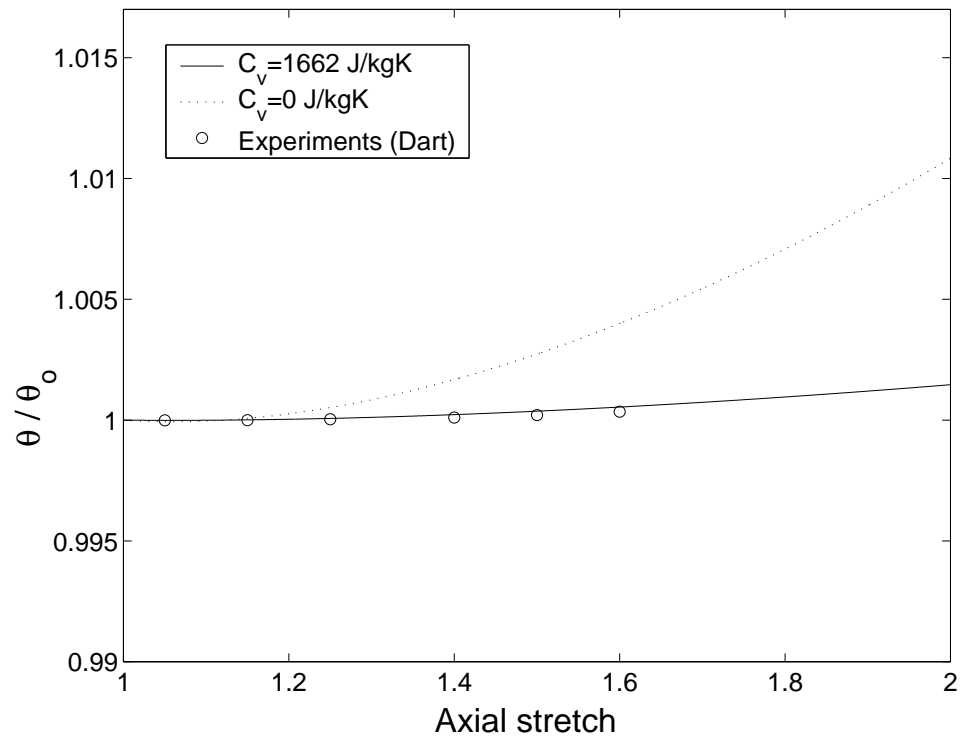


Fig. 9. The variation of temperature with axial stretch, for the different  $C_v$ . Experimental data is from Dart (see James and Guth [84])

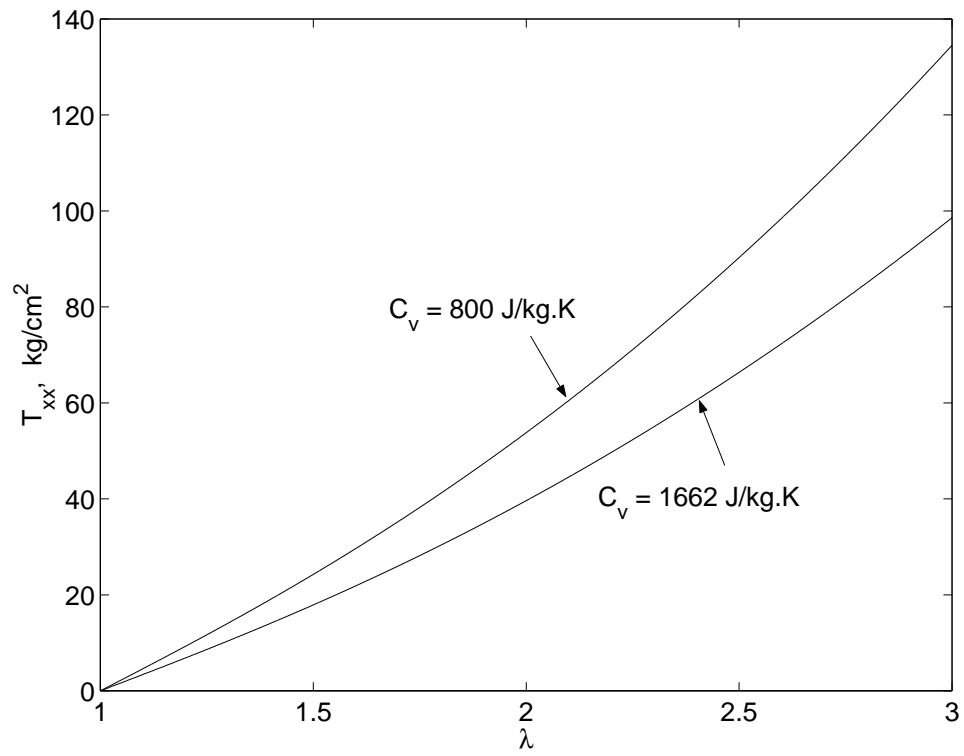


Fig. 10. The variation of axial stress  $\sigma$  with axial stretch, for the different  $C_v$

The stress responses plotted in Figure 10 are very close for the both constrained and unconstrained cases. This implies that the deformation-entropy constraint or the equivalent form of the Helmholtz free energy can be employed without serious error.

#### D. Conclusion

We apply the variational procedure to a closed system consisting of a swollen solid and a surrounding fluid and obtain not only the governing equations and boundary conditions of the system but also the interface conditions between the swollen solid and the surrounding fluid in the equilibrium state. The limiting procedure is applied to the volume additivity constraint and the incompressibility of the surrounding fluid. It helps to identify how materials respond to the constraints. This limiting procedure is also applied to three classes of thermomechanical constraints for a thermoelastic body. It is shown that the deformation-energy constraint and the deformation-entropy constraint are equivalent and that they can be derived from appropriate Helmholtz potentials, which are affine in the absolute temperature. From these results, we conclude that it is unnecessary to consider the deformation-energy and the deformation-entropy relations as constraints. It may be beneficial to employ appropriate Helmholtz potentials to impose these relations to a thermoelastic body.

The variational procedure and the limiting procedure presented in this chapter provide a systematic way to obtain governing equations, boundary conditions, and constraint responses from the constitutive form for the Helmholtz potential function with necessary constraints with respect to all admissible variations of the deformation of the swollen solid and mass flux. In later chapters, this procedure is applied to a swollen rubber, a solution, and a swollen ionic polymer. For the case of a swollen ionic polymer, chemical reactions are also considered as a possible variation at equilibrium.

## CHAPTER IV

MODELING OF THE SWELLING BEHAVIOR OF A POLYMER IN THE  
PRESENCE OF MASS FLUX

The aim of this chapter is to model the swelling behavior of a rubber-like polymer in the presence of slow diffusion of a liquid through the polymer without chemical reactions.

The present approach is based on the consideration of the thermodynamics of dissipative systems and utilizes a variational technique centered around the assumption of maximum rate of dissipation. As we presented in the literature review in chapter II, the origins of this approach dates to the work of Ziegler [72]. Here, we follow the thermodynamic frame work developed by Rajagopal and Srinivasa [51, 55] and Srinivasa [85].

Using the conditions for equilibrium presented in chapter III and a specific form for the Helmholtz potential, we obtain the free swelling equation, which is identical to the Flory-Rehner equation (2.14). Then, we consider the non-equilibrium case. Since we are considering systems at a given fixed temperature, it is an easy matter to identify the rate of dissipation as the difference between the working on the mixture and the rate of increase of the total free energy of the system. Unlike traditional approaches to dissipative systems, we assume a specific constitutive form for the rate of dissipation. The total rate of dissipation is now maximized and the governing equations are obtained.

Finally, the problem of a rubber slab that is immersed in a fluid is investigated and the results compared to the experiments of Paul and Ebra-Lima [75]. Also the hysteresis behavior of the swollen solid for time dependent loads is solved.

A. A special form for the Helmholtz potential and the resulting equilibrium swelling Treloar[32] assumed that the total Helmholtz free energy  $\psi^*$  of the system is equal to the sum of the free energy of mixing  $\psi_m^*$  for a linear polymer and the free energy of network extension  $\psi_e^*$ , i.e.

$$\psi^* = \nu\psi_e^* + \psi_m^*, \quad \left(\nu = \frac{1}{\det\mathbf{F}}\right) \quad (4.1)$$

where  $\nu$  is the volume fraction of rubber in the swollen solid. Although the free energy of fluid  $\psi_f$  in the swollen solid was not mentioned in his work, it appears from a close reading of his work that he tacitly assumed that the free energy fluid at the swollen body is zero. Here, since we consider the fluid as part of the system we shall explicitly consider the fluid free energy. Thus, let us assume the total free energy of the swollen solid as

$$\psi^* = \nu\psi_e^* + \psi_m^* + (1 - \nu)\psi_f. \quad (4.2)$$

In order find a appropriated form for  $\psi_m^*$ , we express the entropy of mixing for the given volume, (2.3) in chapter II, into the function of volume fraction

$$S_m = -\frac{R}{V_o} \left[ (1 - \nu_s)\ln(1 - \nu_s) + \frac{1}{x\nu_s} \ln \frac{\nu_s}{x(1 - \nu_s)} \right] \quad (4.3)$$

If the number of segment of a polymer molecule  $x$  is sufficiently large, then the second term of (4.3) may be ignored. Using the heat of dilution (2.5) in chapter II, the free energy of mixing is given as

$$\psi_m^* = \frac{RT}{V_o} ((1 - \nu)\ln(1 - \nu) - \chi\nu^2). \quad (4.4)$$

Thus, we set

$$\psi^* = \frac{\nu\rho_{mo}RT}{2M} (I_1 - 3) + \frac{RT}{V_o} ((1 - \nu)\ln(1 - \nu) - \chi\nu^2) + (1 - \nu)\psi_f. \quad (4.5)$$



where  $I_1 = \text{tr}(\mathbf{F}\mathbf{F}^T)$ ,  $\nu = 1/\det\mathbf{F}$ ,  $R$  is the gas constant,  $T$  the absolute temperature of the swollen solid,  $M$ , the molecular weight between cross-links of solid,  $V_o$  the molar volume of the fluid, and  $\chi$  a mixing parameter on the particular solid-fluid combination. Then, substituting (4.5) into (3.49), the Helmholtz free energy  $\psi_f$  of the fluid is eliminated and the equation for the homogeneously swollen polymer is derived as

$$g(\nu) = \frac{RT}{V_o}(\ln(1 - \nu) + \nu + \chi\nu^2) + \frac{\rho_{mo}RT}{M}\nu^{\frac{1}{3}} = -p. \quad (4.6)$$

where the additional traction  $\mathbf{t}$  on the boundary of the swollen solid is assumed to be  $-p\mathbf{n}_1$ . It should be noted that the hydrostatic pressure  $-p$  is the additional force on the boundary of the swollen solid. This result is the same as that of Treloar [32, p.146] and shows that the swelling is independent of the pressure  $P_\infty$  of the surrounding fluid. For the particular case of  $p = 0$ , corresponding to free swelling, this reduces to

$$g(\nu) = 0. \quad (4.7)$$

The form (4.7) has been found by Gee [36] to account satisfactorily for the swelling behavior of a series of differently cross-linked natural rubbers, the value of  $M$  which is related to the degree of cross linking.  $g(\nu)$  is plotted in figure 11 for the different value of  $M$ (different vulcanization). Note that the equation (4.6) can have no root or two roots for free swelling and tensile traction on the boundary of the swollen solid.

If the formula derived by Flory for the elastic network entropy (Flory and Rehner [37], Treloar [32, p. 76, 136]) were used for  $\psi_e^*$  of (4.1), we would have to replace (4.5) by

$$\psi^* = \frac{\nu\rho_{mo}RT}{2M}(I_1 - 3 + \ln\nu) + \frac{RT}{V_o}((1 - \nu)\ln(1 - \nu) - \chi\nu^2) + (1 - \nu)\psi_f. \quad (4.8)$$

Then, the condition for equilibrium swelling with additional traction  $-p\mathbf{n}_1$  on the

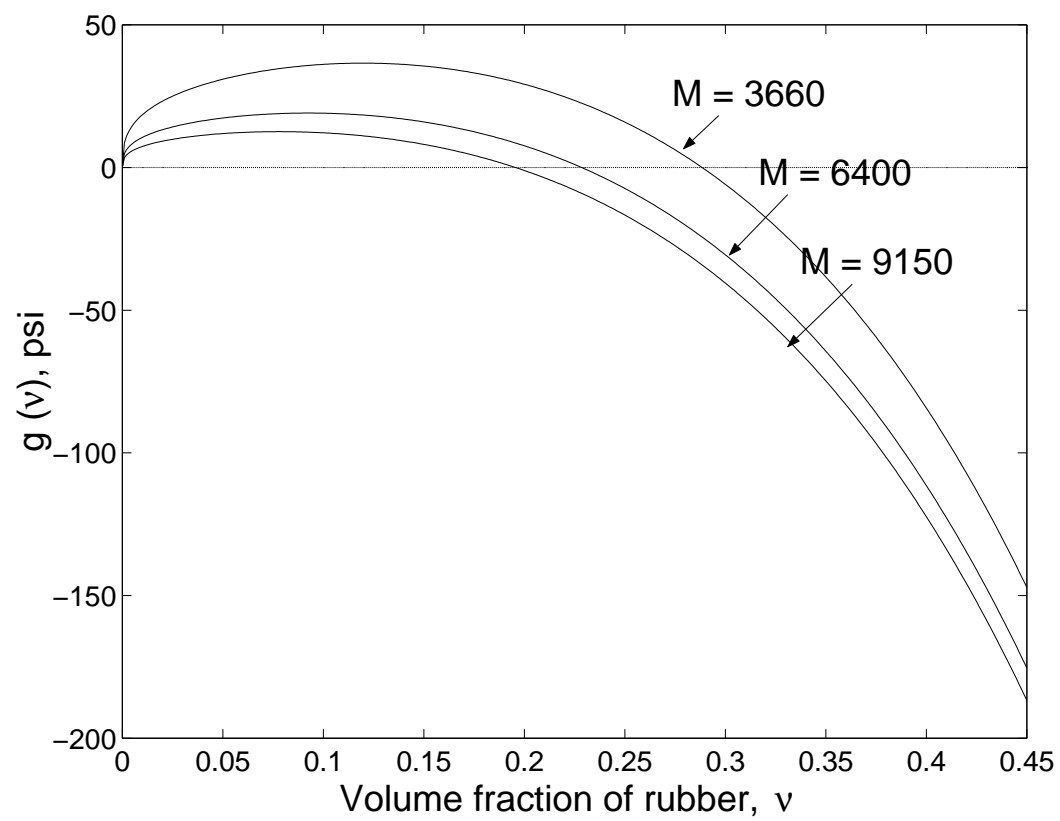


Fig. 11. Free swelling for different values of  $M$  (gm/mol)

boundary of the swollen solid would become

$$\frac{RT}{V_o}(\ln(1 - \nu) + \nu + \chi\nu^2) + \frac{\rho_{mo}RT}{M}\left(\nu^{\frac{1}{3}} - \frac{\nu}{2}\right) = -p. \quad (4.9)$$

which is the same as the Flory-Rehner equation (2.14).

The above analysis demonstrates that the variational procedure used above, results in the same equations as derived by Treloar and by Flory and Rehner, but provides additional insight into the nature of the additional boundary conditions that are generated.

#### B. Dissipative process in the swollen solid

Physically, diffusion can be explained as a random movement of atomic scale particles through other particles, called Brownian motion. These random movement rise to a continual mixing of components and are the cause of changes in concentration, whose rate can be measured on a macroscopic scale. From a microscopic viewpoint, the drag on the flowing fluid is caused by the Brownian motion of the fluid molecules (see Doi [86]) and the drag force causes dissipation.

In a thermomechanical process, work done on the system is either stored as the stored energy or dissipated. Rajagopal and Srinivasa [52] defined a rate of dissipation function as the function representing the rate of conversion of the mechanical power supplied into heat. The rate of dissipation is non-negative for all processes that the material is capable of undergoing. In an isothermal process of the energy balance equation then stipulates that the rate of dissipation is equal to the difference between the ratio of work and the rate of change of the Helmholtz potential.

### 1. Assumption of maximum rate of dissipation

As the fluid flows through the swollen solid, work is done by the external traction on the body. The difference between the power of the boundary tractions and the rate of increase of the total Helmholtz potential of the swollen solid must be equal to the rate of mechanical energy dissipated, i.e.,

$$- \int_{\Gamma_f} P_\infty \mathbf{n}_2 \cdot \mathbf{v}_f dA + \int_{\Gamma_m} \mathbf{t} \cdot \mathbf{v}_m dA - \frac{d\Psi}{dt} := \Sigma \quad (4.10)$$

where  $\Sigma$  is the total rate of dissipation.

Now we substitute the form (3.12) for  $\Psi$  and expand the resulting expression to get

$$\begin{aligned} \left( \frac{d\Psi}{dt} \right)_{\text{in } \Omega_m} &= \int_{\Omega_m} \left( \left[ -\text{div} \left( \frac{\partial \psi^*}{\partial \mathbf{F}} \mathbf{F}^T \right) + \text{grad} \left( (\phi + \rho_{fo}) \frac{\partial \psi^*}{\partial \phi} - \psi^* \right) \right] \cdot \mathbf{v}_m \right. \\ &+ \left. \text{grad} \left( \frac{\partial \psi^*}{\partial \phi} \right) \cdot \mathbf{q} \right) dV \\ &+ \int_{\Gamma_m} \left( \left[ \frac{\partial \psi^*}{\partial \mathbf{F}} \mathbf{F}^T + (\psi^* - (\phi + \rho_{fo}) \frac{\partial \psi^*}{\partial \phi} - \psi_f + \rho_f \frac{\partial \psi_f}{\partial \rho_f}) \mathbf{I} \right] \mathbf{v}_m \right. \\ &- \left. \left( \frac{\partial \psi^*}{\partial \phi} - \frac{\partial \psi_f}{\partial \rho_f} \right) \mathbf{q} \right) \cdot \mathbf{n}_1 dA. \end{aligned} \quad (4.11)$$

Then, the total rate of dissipation  $\Sigma_m$  in  $\Omega_m$  is given by

$$\begin{aligned} \Sigma_m &= \int_{\Omega_m} \left( \text{div} (\hat{\mathbf{T}}) \cdot \mathbf{v}_m - \text{grad} (K_m) \cdot \mathbf{q} \right) dV \\ &+ \int_{\Gamma_m} \left( - \left[ \hat{\mathbf{T}} + (\rho_f K_f - \psi_f) \mathbf{I} \right] \mathbf{v}_m \cdot \mathbf{n}_1 + (K_m - K_f) \mathbf{q} \cdot \mathbf{n}_1 + \mathbf{t} \cdot \mathbf{v}_m \right) dA \end{aligned} \quad (4.12)$$

where  $K_m$ ,  $K_f$  and  $\hat{\mathbf{T}}$  are defined at (3.25), and (3.35), respectively.

### 2. The bulk dissipation and the saturation boundary condition

Typically (4.10) is stated in the form of an inequality, which is used to obtain restrictions on constitutive relations. But in this work, we will follow Ziegler [72] and

Rajagopal and Srinivasa [52, 55] and postulate a constitutive form for the rate of dissipation. A closer look of (4.10) reveals that the equations can be divided into equations for the volume element and equations for the surface. This implies that the dissipation takes place in the volume and on the boundary of the system. Each of terms of the rate of dissipation vanishes independently for non-dissipative process—a fact that may be verified by substituting the governing equations derived for non-dissipative processes (3.26)–(3.31) into the above expression. We now identify the bulk rates of specific dissipation  $\xi_{(b)}$  and surface rate of specific dissipation  $\xi_{(s)}$  as

$$\begin{aligned}\Sigma_m &= \int_{\Omega_m} \xi_{(b)} dV + \int_{\Gamma_m} \xi_{(s)} dA \\ \xi_{(b)} &= \operatorname{div}(\hat{\mathbf{T}}) \cdot \mathbf{v}_m - \operatorname{grad}(K_m) \cdot \mathbf{q}. \\ \xi_{(s)} &= -(\hat{\mathbf{T}} + (\rho_f K_f - \psi_f)\mathbf{I})\mathbf{v}_m \cdot \mathbf{n}_1 + (K_m - K_f)\mathbf{q} \cdot \mathbf{n}_1 + \mathbf{t} \cdot \mathbf{v}_m.\end{aligned}\tag{4.13}$$

Clearly, since diffusion is a dissipative process, we shall assume that the bulk rate of dissipation is a non-zero function of the density of the two constituents, the deformation of the swollen rubber and the mass flux of the fluid, in the form

$$\xi_{(b)} = \hat{\xi}(\rho_m, \mathbf{q}, \mathbf{F}).\tag{4.14}$$

Now we assume that unlike the bulk of the material, the boundary of the swollen material is saturated so that the surface dissipation vanishes. i.e.,

$$\xi_{(s)} = 0\tag{4.15}$$

Now, we shall invoke the assumption of maximum rate of dissipation (Rajagopal and Srinivasa [55], Baek and Srinivasa [81], and Ziegler [72]) and stipulate that the diffusion proceeds in such a way as to extremize the rate of dissipation  $\Sigma_m$  subject to the constraints (4.13) and (4.14). To carry out this maximization, we introduce

the auxiliary function,  $\tilde{\Sigma}$  using the technique of Lagrange multiplier subject to the constraint(4.13) by

$$\tilde{\Sigma} := \Sigma_m + \int_{\Omega_m} \lambda \left( \xi + \text{div}(\hat{\mathbf{T}}) \cdot \mathbf{v}_m - \text{grad}(K_m) \cdot \mathbf{q} \right) dV \quad (4.16)$$

where  $\xi = \xi_{(b)}$ . Extremizing  $\tilde{\Sigma}$  over the set of all kinematically admissible velocity field and the fluid flux field, and taking the limit of volume additivity, the general field equations for dissipative process are delivered as

$$\text{div} \left( \frac{\partial \psi^*}{\partial \mathbf{F}} \mathbf{F}^T - (\rho_{fo} K_m - \psi^*) \mathbf{I} \right) = 0 \quad \text{in } \Omega_m \quad (4.17)$$

$$\text{grad}(K_m) = \tilde{\lambda} \frac{\partial \xi}{\partial \mathbf{q}}, \quad \text{in } \Omega_m \quad (4.18)$$

where  $\tilde{\lambda} = \lambda/(1 - \lambda)$ . Then, taking inner product of (4.18) with  $\mathbf{q}$  and using (4.13) and (4.17),  $\tilde{\lambda}$  is obtained as

$$\tilde{\lambda} = \frac{-\xi}{\frac{\partial \xi}{\partial \mathbf{q}} \cdot \mathbf{q}}. \quad (4.19)$$

The interfacial boundary conditions are obtained as

$$\left[ \frac{\partial \psi^*}{\partial \mathbf{F}} \mathbf{F}^T - (\rho_{fo} K_m - \psi^*) \mathbf{I} \right] \mathbf{n}_1 = \mathbf{t} - P_f \mathbf{n}_1 \quad \text{on } \Gamma_m \quad (4.20)$$

$$K_m = K_f \quad \text{on } \Gamma_m \quad (4.21)$$

Again we see that the chemical potential is continuous across the boundary.

The complete set of equations for the diffusion of the fluid into the polymer together with the definitions for the chemical potentials and the volume additivity constraint are summarized in Table III.

At first glance the equations seem to be completely different from that derived from mixture theory (see Rajagopal and Tao[44]) and specialized for the current conditions. Specifically, the equations derived in the theory of mixtures appears to be much more complicated in form when compared to the current approach. However,

Table III. Summary of equations for the diffusion of the fluid into the polymer

DESCRIPTION	EQUATIONS
Conservation of mass	$\frac{\partial \rho_m}{\partial t} + \text{div}(\rho_m \mathbf{v}_m) + \text{div} \mathbf{q} = 0, \quad \text{in } \Omega_m$ $\rho_f = \text{constant}, \quad \text{in } \Omega_f$
Volume additivity constraint	$\phi = \rho_m - \rho_{fo} - \frac{\rho_{mo} - \rho_{fo}}{J} = 0$
Helmholtz potential and rate of dissipation function	$\psi^* = \psi^*(\mathbf{F}) = \nu \psi_e + (1 - \nu) \psi_f + \psi_{\text{mix}}$ $\psi_f = \text{constant for isothermal process}$ $\xi = \xi(\rho_m, \mathbf{q})$
Chemical potentials	$K_m = \text{arbitrary finite}$ $K_f = \frac{P_f + \psi_f}{\rho_{fo}}, \quad (P_f = \text{arbitrary finite})$
Field equations	$\text{div} \left( \frac{\partial \psi^*}{\partial \mathbf{F}} \mathbf{F}^T - (\rho_{fo} K_m - \psi^*) \mathbf{I} \right) = 0 \quad \text{in } \Omega_m$ $\text{grad}(K_m) = \tilde{\lambda} \frac{\partial \xi}{\partial \mathbf{q}} \quad \text{in } \Omega_m$ $\text{grad}(P_f) = 0 \quad \text{in } \Omega_f$ <p>( where <math>\tilde{\lambda} = -\xi / (\frac{\partial \xi}{\partial \mathbf{q}} \cdot \mathbf{q})</math> )</p>
Boundary conditions	$\left[ \frac{\partial \psi^*}{\partial \mathbf{F}} \mathbf{F}^T - (\rho_{fo} K_m - \psi^*) \mathbf{I} \right] \mathbf{n} = \mathbf{t} - P_f \mathbf{n} \quad \text{on } \Gamma_m$ $K_m = K_f \quad \text{on } \Gamma_m$ $P_f = P_\infty \quad \text{on } \Gamma_f$

careful scrutiny of the mixture equations together with a redefinition of the constraint pressure will show that the mixture theory form is exactly equivalent to the form presented here. This is shown in Appendix B. Note that in the current version, there is a clear identification of the constraint term as the limiting form of the chemical potential, a fact that is not evident in the mixture theory format. Also, the present approach utilizing the maximization of the rate of dissipation also provides the required additional boundary condition that is lacking in mixture theory. It also provides a clear rationale for the boundary condition.

To complete the specification of the problem, it remains to specify the form of the dissipative response, specifically the rate of dissipation function. From a microscopic viewpoint, the drag on the flowing fluid arises due to the Brownian motion of the networks in the fluid, and based on experimental data (see Doi [86, p. 157]), it can be argued that the drag force decreases rapidly with increasing fluid concentration. Such a dependence on the fluid concentration has been clearly demonstrated for the case of solutions of uncross linked polymers in solvents over a wide range of molecular weights and solvents. Motivated by this, we shall assume that the rate of dissipation associated with the diffusion is of the form

$$\xi = k\gamma^n \mathbf{q} \cdot \mathbf{q}, \quad n > 0, \quad (4.22)$$

where  $k$  is constant and  $\gamma$  is given by

$$\gamma = \frac{\rho_{fo} - \rho_m}{\rho_m - \rho_{so}} = \frac{1}{J - 1}. \quad (4.23)$$

Now substitution of (4.22) into (4.19) gives  $\tilde{\lambda} = -1/2$ . Also substitution of the value of  $\tilde{\lambda}$  and (4.22) into (4.18) reveals that

$$\text{grad}(K_m) = -k\gamma^n \mathbf{q}. \quad (4.24)$$



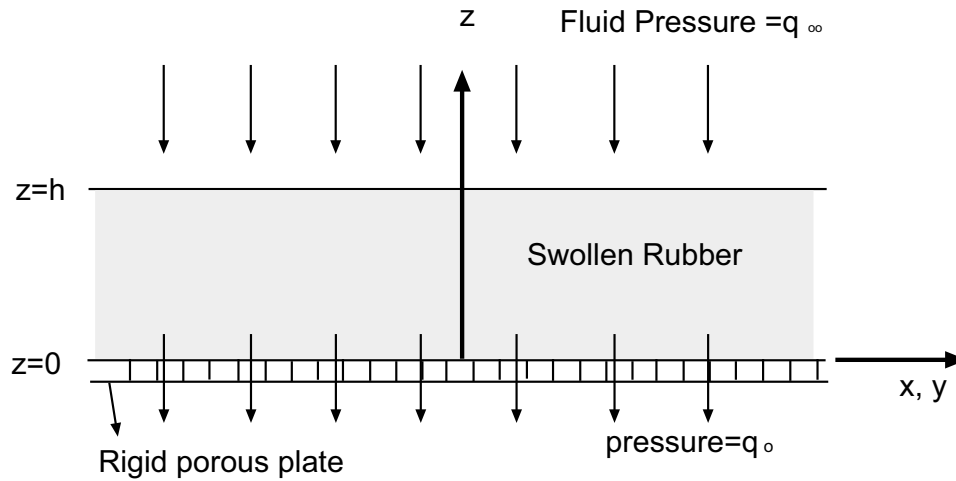


Fig. 12. Schematic view of the current configuration for diffusion through a rubber sheet

We note that the form of the drag force utilized here is quite different from that used by Shi *et al.* [45].

### C. Diffusion of toluene through pure gum rubber sheet

We shall illustrate the predictions of the theory and compare it with observations by considering the steady-state diffusion of an ideal fluid in the direction normal to the surface of an isotropic non-linear elastic layer. We shall compare the predicted solution to the measured diffusion of toluene and other solvents into pure rubber. Figure 12 shows the current state of the layer. We refer to the plane  $z = h$  as the upstream surface and  $z = 0$  which is fixed to a rigid porous plate as the downstream surface. The initial position of a particle of the solid is at  $(X, Y, Z)$  and its current position is  $(x, y, z)$ . The planes defining the upstream surface and downstream surface are given by  $Z = 0$  and  $Z = H_0$ . Its deformation is given by

$$x = \eta X, \quad y = \eta Y, \quad z = f(Z) \quad (4.25)$$

where  $\eta$  is a constant. The volume fraction of the solid  $\nu$  is given by

$$\nu = \frac{1}{\eta^2 f'} \quad (4.26)$$

where  $(\cdot)'$  denotes the derivative with respect to  $Z$ . The flux  $\mathbf{q}$  is constant and acts only in the  $z$  direction. Using (4.5) and (4.24), the equation of motion (4.17)(4.18) reduce to the following forms

$$\left( \frac{\rho_{mo}RT}{M} \nu f'^2 + \frac{RT}{V_o} (\ln(1 - \nu) + \nu + \chi\nu^2) - \rho_{fo}K_m + \psi_f \right)' = 0 \quad (4.27)$$

$$(K_m)' = \frac{-kf'q}{(\eta^2 f' - 1)^n} \quad (4.28)$$

The fluid pressure upstream and downstream are  $q_\infty$  and  $q_o$  respectively, and the traction on the upper surface of the swollen solid is zero and the traction on the bottom surface is unknown (denoted by  $t$ ), then the boundary conditions at  $Z = H_o$  are

$$\frac{\rho_{mo}RT}{M} \nu f'^2 + \frac{RT}{V_o} (\ln(1 - \nu) + \nu + \chi\nu^2) - \rho_{fo}K_m + \psi_f = -P_\infty \quad (4.29)$$

$$K_m = \frac{1}{\rho_{fo}} (P_\infty + \psi_f) \quad (4.30)$$

and the conditions at  $Z = 0$  are

$$\frac{\rho_{mo}RT}{M} \nu f'^2 + \frac{RT}{V_o} (\ln(1 - \nu) + \nu + \chi\nu^2) - \rho_{fo}K_m + \psi_f = t - P_o \quad (4.31)$$

$$K_m = \frac{1}{\rho_{fo}} (P_o + \psi_f) \quad (4.32)$$

$$f(0) = 0 \quad (4.33)$$

The differential equation (4.27) implies that the right hand sides of the boundary conditions (4.29) and (4.31) are equal. i.e.,

$$t = -(P_\infty - P_o). \quad (4.34)$$

In order to get rid of constant term  $\psi_f$ , let us define  $\hat{P} = \rho_{fo}K_m - \psi_f$ , then the equations simplify to

$$\left(\frac{\rho_{mo}RT}{M}\nu f'^2 + \frac{RT}{V_o}(\ln(1 - \nu) + \nu + \chi\nu^2) - \hat{P}\right)' = 0 \quad (4.35)$$

$$(\hat{P})' = \frac{-\alpha f'q}{(\eta^2 f' - 1)^n} \quad (4.36)$$

where  $\alpha = \rho_{fo}k$ . The boundary conditions at  $Z = H_o$  reduce to

$$\frac{\rho_{mo}RT}{M}\nu f'^2 + \frac{RT}{V_o}(\ln(1 - \nu) + \nu + \chi\nu^2) - \hat{P} = -P_\infty \quad (4.37)$$

$$\hat{P} = P_\infty \quad (4.38)$$

and the boundary conditions at  $Z = 0$  become

$$\frac{\rho_{mo}RT}{M}\nu f'^2 + \frac{RT}{V_o}(\ln(1 - \nu) + \nu + \chi\nu^2) - \hat{P} = -P_\infty \quad (4.39)$$

$$\hat{P} = P_o \quad (4.40)$$

For computation, the membrane is taken as gum rubber and the fluid as toluene. In view of the fact that the membrane is placed in a chamber with hard lateral walls, we shall assume that there is no lateral expansion, so that  $\eta = 1$ . The material constants are obtained from Paul and Ebra-Lima [75]:  $\rho_{mo}=0.862$  gm/c.c,  $\rho_{fo}=0.869$  gm/c.c,  $V_o=106$  c.c/mole,  $M=9151$  gm/mole and  $\chi=0.425$ . The gas constant  $R = 8.317 \times 10^7$  dyne-cm/mole-°K. Taking room temperature to be 30°C, we get  $T=303.16$  °K. We set initial membrane thickness  $H_o= 0.0265$  cm. The values  $n = 3$  and  $\alpha = 9 \times 10^7$  dyne.day.gm/cc were selected. On solving (4.35) and (4.36) with boundary conditions (4.37), (4.38), (4.39) and (4.40) numerically, we obtained a negative value for the flux  $q$  which means that the flux is in the the negative z-direction. The numerical result is plotted on a flux-pressure difference graph as shown in Fig.13. The experimental data obtained by Paul and Ebra-Lima [75] is indicated by open circles. The numerical

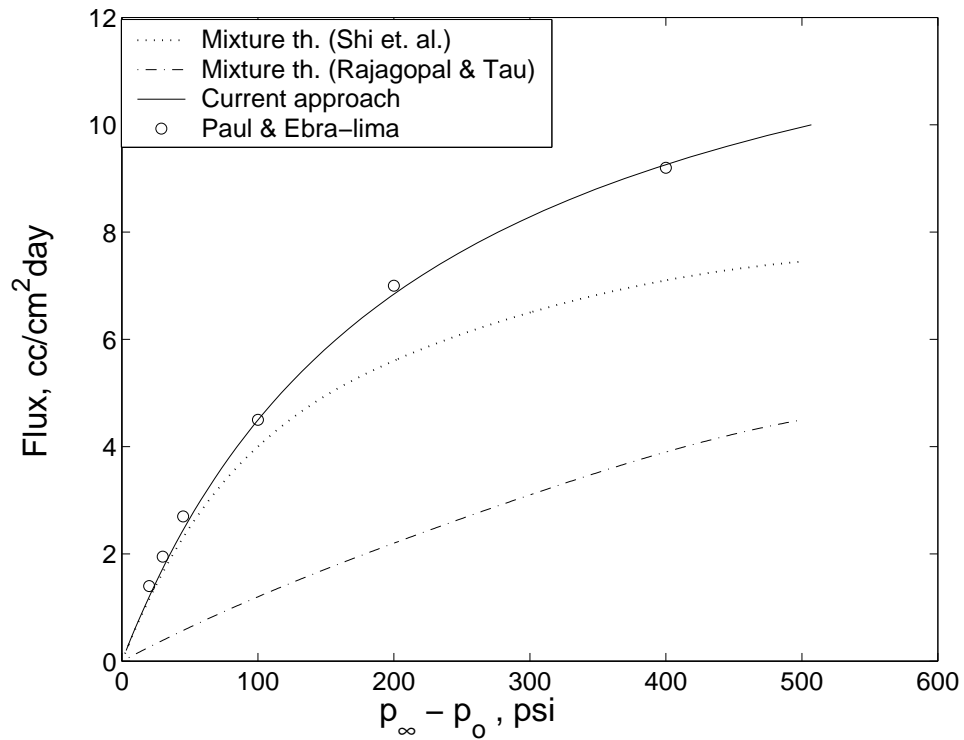


Fig. 13. Comparison of flux-pressure difference relations for toluene between (a) mixture theory 1: saturated boundary condition (Shi *et al.* [45]), (b) mixture theory 2: split traction boundary condition (Rajagopal and Tao [44]), (c) experimental data by Paul and Ebra-Lima [75], (d) current approach for the form of Helmholtz free energy (4.5) of mixture;  $n=3$ ,  $\eta = 1$ ,  $\alpha = 9 \times 10^7$  dyne.day.gm/cc

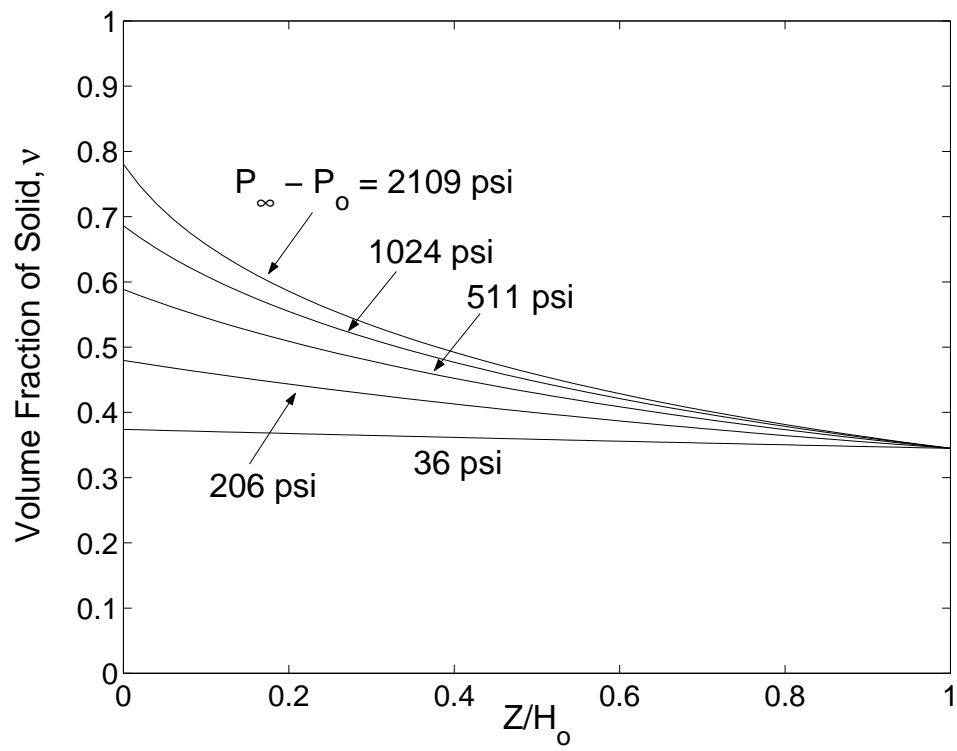


Fig. 14. Variation of volume fraction of solid through layer thickness for various values of pressure difference

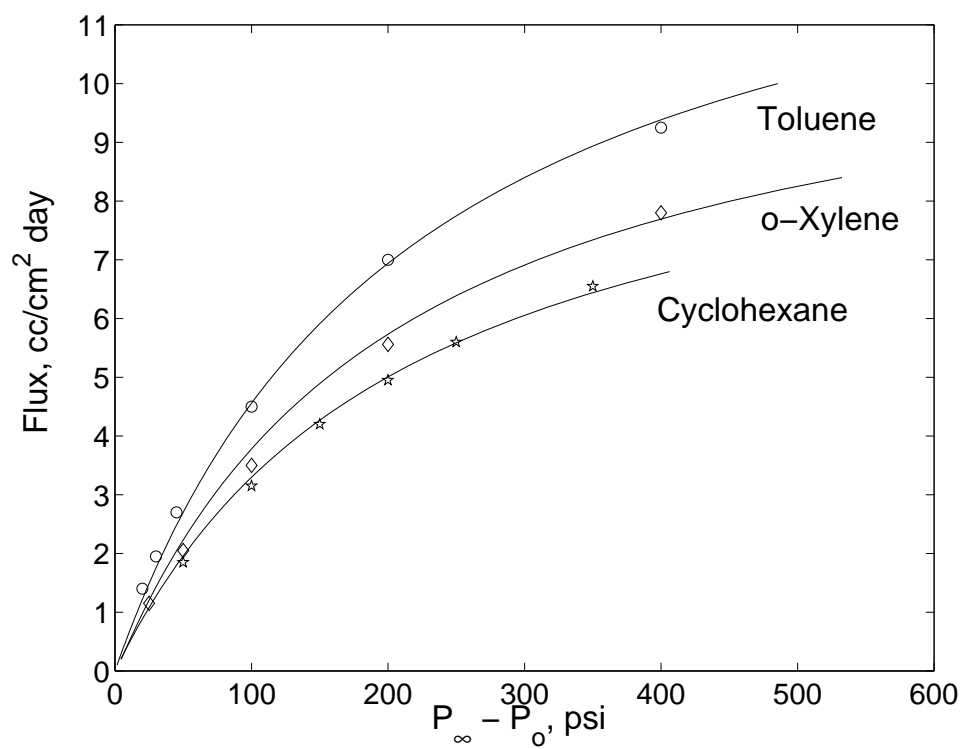


Fig. 15. Comparison of numerical results with experimental results of Paul and Ebra-Lima [75] for toluene, o-xylene, and cyclohexane. The free energy function (4.5) is used here

result of mixture theory (Rajagopal and Tao [44]) is also plotted for comparison.

Furthermore, it can be seen from Figure 13 that the mass flux of the fluid becomes less sensitive to the pressure difference at higher values of the pressure difference. This phenomenon can be explained by Figure 14. When the pressure difference increases, the traction on the bottom layer of the mixture due to the plate increases. Hence, the volume fraction of the solid increases and prevents the flux from increasing, since the flux is quite sensitive to the solid volume fraction.

In Figure 15 we plot numerical results for three different organic liquids, Toluene, o-Xylene, and Cyclohexane. We obtain remarkable agreement with the experiments of Paul and Ebra-Lima [75]. Material constants of liquids are the same as those obtained by experiments: for o-Xylene -  $\rho_{fo}=0.88$  gm/c.c,  $V_o=118.4$  c.c/mole, and  $\chi=0.408$ , for Cyclohexane -  $\rho_{fo}=0.779$  gm/c.c,  $V_o=108$  c.c/mole, and  $\chi=0.448$ . The value of  $\alpha$  was set to  $1.0 \times 10^8$  dyne.day.gm/cc and  $1.1 \times 10^8$  dyne.day.gm/cc for o-Xylene and Cyclohexane, respectively, to match the numerical curve to the experimental curve.  $n$  was set to 3 for all three liquids.

#### D. Time dependent load and hysteresis

In the previous sections in this chapter, we investigated the steady state diffusion problem under constant traction on the surface of the swollen solid and constant hydrostatic pressure of the surrounding fluid. In this section we model the behavior of swollen solid subject to time dependent loads. When the traction condition is changed, it takes time to reach a equilibrium state due to the dissipative nature of diffusion. A schematic representation of the swollen solid system with time dependent loads is shown in Figure 16. The tractions  $F_t$  on its upstream surface ( $Z = H_o$ ) and downstream surface ( $Z = -H_o$ ) are equal in magnitude but opposite direction. The

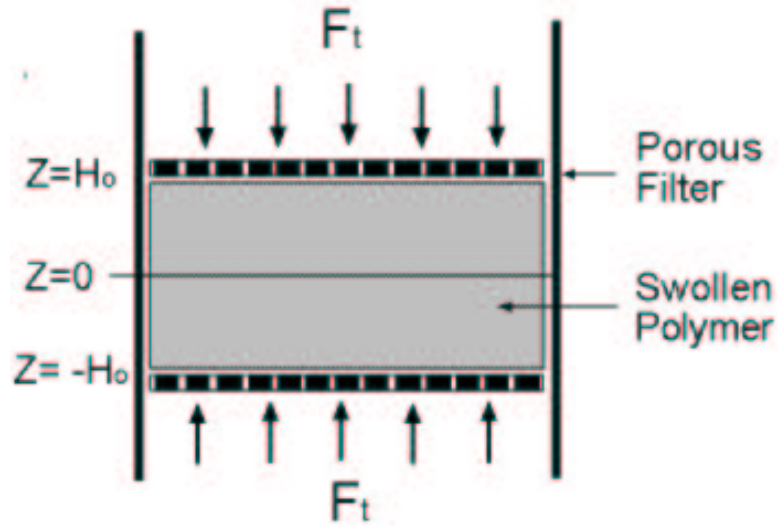


Fig. 16. Schematic representation of a system with time dependent traction condition initial position of a particle of the swollen solid is  $(X, Y, Z)$  and its current position is  $(x, y, z)$ . The planes of upstream surface and middle plane in Figure 16 are given by  $Z = H_o$  and  $Z = 0$  and the deformation of the swollen solid body is defined by

$$x = X, \quad y = Y, \quad z = f(Z). \quad (4.41)$$

The  $\mathbf{F}$  and  $\mathbf{B}$  are calculated from the deformation as

$$\mathbf{F} = \text{Dia}\{1, 1, f'\}, \quad \mathbf{B} = \text{Dia}\{1, 1, (f')^2\} \quad (4.42)$$

where  $(\cdot)'$  denotes the derivative with respect to  $Z$ . The volume fraction of the solid  $\nu$  is given by

$$\nu = \frac{1}{f'}. \quad (4.43)$$

The flux  $\mathbf{q}$  is given by

$$\mathbf{q} = \{0, 0, q\}. \quad (4.44)$$



For an arbitrary scalar variable  $\phi = \hat{\phi}(z, t) = \tilde{\phi}(Z, t)$ , we have the following relations

$$\dot{\phi} = \frac{\partial \phi}{\partial t} + \text{grad} \phi \mathbf{v}, \quad \frac{\partial \phi}{\partial z} = \frac{1}{f'}(\phi)' \quad (4.45)$$

where the supper script dot denotes the material time derivative and  $(\cdot)'$  denote the derivative with respect to  $Z$ . Using the above relations and deformation fields, the equation of conservation of mass (3.3) reduces to

$$\dot{\rho} + \frac{\rho}{f'}(\dot{f})' + \frac{q'}{f'} = 0 \quad (4.46)$$

and the time derivative of the volume additivity equation (3.6) becomes

$$\dot{\rho} = -\frac{(\rho_o - \rho_{fo})(\dot{f})'}{(f')^2} \quad (4.47)$$

Substituting (3.6) and (4.47) into (4.46) gives

$$\rho_{fo}(\dot{f})' + q' = 0 \quad (4.48)$$

Using the relations (4.45) and the deformation field (4.42), the field equations (4.17) and (4.18) become

$$\left( \frac{\rho_o RT}{M} f' + \frac{RT}{V_o} (\ln(1 - (f')^{-1}) + (f')^{-1} + \chi(f')^{-2}) - \rho_{fo} \hat{K} \right)' = 0 \quad (4.49)$$

$$\hat{K}' = \frac{-k f' q}{(f' - 1)^3} \quad (4.50)$$

$$\rho_{fo}(\dot{f})' + q' = 0 \quad (4.51)$$

Boundary conditions are

$$\frac{\rho_o RT}{M} f' + \frac{RT}{V_o} (\ln(1 - (f')^{-1}) + (f')^{-1} + \chi(f')^{-2}) - \rho_{fo} \hat{K} = -F_t - P_\infty \quad (4.52)$$

$$\hat{K} = \frac{P_\infty}{\rho_{fo}} \quad \text{at } Z = Z_o \quad (4.53)$$

$$f'' = 0 \quad \text{at } Z = 0. \quad (4.54)$$

where  $F_t$  is compressive normal stress in z-direction. From the equation (4.49) and the boundary condition (4.52), we obtain an equation for the system as

$$\frac{\rho_o RT}{M} f' + \frac{RT}{V_o} (\ln(1 - (f')^{-1}) + (f')^{-1} + \chi(f')^{-2}) - \rho_{fo} \hat{K} = -F_t - P_\infty \quad (4.55)$$

Differentiating (4.50) with respect to  $Z$  and substituting this into (4.51), we obtain

$$\left[ \frac{(f' - 1)^3}{k f'} \right] \hat{K}'' + \left[ \frac{(f' - 1)^2 (2f' + 1) f''}{k (f')^2} \right] \hat{K}' - \rho_{fo} (\dot{f})' = 0 \quad (4.56)$$

Spatial derivatives of  $\hat{K}$  obtained by differentiating (4.55) with respect to  $Z$  are

$$\hat{K}' = \frac{RT}{\rho_{fo}} \left[ \frac{\rho_o}{M} + \frac{1}{V_o} \left( \frac{1}{(f')^2 - f'} - \frac{1}{(f')^2} - \frac{2\chi}{(f')^3} \right) \right] f'' \quad (4.57)$$

$$\begin{aligned} \hat{K}'' &= \frac{RT}{\rho_{fo}} \left[ \frac{\rho_o}{M} + \frac{1}{V_o} \left( \frac{1}{(f')^2 - f'} - \frac{1}{(f')^2} - \frac{2\chi}{(f')^3} \right) \right] f''' \\ &+ \frac{RT}{\rho_{fo} V_o} \left[ -\frac{(2f' - 1)}{(f')^2 (f' - 1)^2} + \frac{2}{(f')^3} + \frac{6\chi}{(f')^4} \right] (f'')^2 \end{aligned} \quad (4.58)$$

Substituting (4.57) and (4.58) into (4.56), we get the following non-linear equation involving  $f'$  and its higher order terms

$$g_1 f''' + g_2 f'' + g_3 \dot{f}' = 0 \quad (4.59)$$

where

$$g_1 = \frac{(f' - 1)^3}{f'} \left[ \frac{\rho_o}{\rho_{fo}} + \frac{M}{\rho_{fo} V_o} \left( \frac{1}{(f')^2 - f'} - \frac{1}{(f')^2} - \frac{2\chi}{(f')^3} \right) \right] \quad (4.60)$$

$$\begin{aligned} g_2 &= \frac{M}{\rho_{fo} V_o} \frac{(f' - 1)^3 f''}{f'} \left[ -\frac{(2f' - 1)}{(f')^2 (f' - 1)^2} + \frac{2}{(f')^3} + \frac{6\chi}{(f')^4} \right] \\ &+ \frac{f''}{f'} \left( \frac{(f' - 1)^2 (2f' + 1)}{f'} \right) \left[ \frac{\rho_o}{\rho_{fo}} + \frac{M}{\rho_{fo} V_o} \left( \frac{1}{(f')^2 - f'} - \frac{1}{(f')^2} - \frac{2\chi}{(f')^3} \right) \right] \end{aligned} \quad (4.61)$$

$$g_3 = -\frac{k \rho_{fo} M}{RT} \quad (4.62)$$

We define the following non-dimensional variables

$$\hat{Z} = \frac{Z}{H_o}, \quad \hat{f} = \frac{f}{H_o}, \quad \hat{t} = \frac{t}{t_s} \quad (4.63)$$

Then, the equation (4.59) becomes

$$\hat{g}_1 \hat{f}''' + \hat{g}_2 \hat{f}'' + \hat{g}_3 \hat{f}' = 0 \quad (4.64)$$

where

$$\hat{g}_1 = \frac{(\hat{f}' - 1)^3}{\hat{f}'} \left[ 1 + \alpha_1 \left( \frac{1}{(\hat{f}')^2 - \hat{f}'} - \frac{1}{(\hat{f}')^2} - \frac{2\chi}{(\hat{f}')^3} \right) \right] \quad (4.65)$$

$$\begin{aligned} \hat{g}_2 = & \alpha_1 \frac{(\hat{f}' - 1)^3 \hat{f}''}{\hat{f}'} \left[ -\frac{(2\hat{f}' - 1)}{(\hat{f}')^2 (\hat{f}' - 1)^2} + \frac{2}{(\hat{f}')^3} + \frac{6\chi}{(\hat{f}')^4} \right] \\ & + \frac{\hat{f}''}{\hat{f}'} \left( \frac{(\hat{f}' - 1)^2 (2\hat{f}' + 1)}{\hat{f}'} \right) \left[ 1 + \alpha_1 \left( \frac{1}{(\hat{f}')^2 - \hat{f}'} - \frac{1}{(\hat{f}')^2} - \frac{2\chi}{(\hat{f}')^3} \right) \right] \end{aligned} \quad (4.66)$$

$$\hat{g}_3 = -\alpha_2. \quad (4.67)$$

Non-dimensional material constants  $\alpha_1$  and  $\alpha_2$  in the above equations are given by

$$\alpha_1 = \frac{M}{\rho_o V_o}, \quad \alpha_2 = \frac{kM(\rho_{fo} H_o)^2}{t_s \rho_o RT} \quad (4.68)$$

Boundary conditions become

$$\hat{f}' + \alpha_1 \left( \ln(1 - (\hat{f}')^{-1}) + (\hat{f}')^{-1} + \chi (\hat{f}')^{-2} \right) = -\hat{F}_t \quad \text{at } \hat{Z} = 1 \quad (4.69)$$

$$f'' = 0 \quad \text{at } \hat{Z} = 0 \quad (4.70)$$

where

$$\hat{F}_t = \frac{MF_t}{\rho_o RT}. \quad (4.71)$$

Since the swollen solid is initially assumed to be in equilibrium, the initial condition are found from equilibrium conditions

$$\hat{f}' + \alpha_1 \left( \ln(1 - (\hat{f}')^{-1}) + (\hat{f}')^{-1} + \chi(\hat{f}')^{-2} \right) = -\hat{F}_{t_o} \quad \text{at } t = t_o \quad (4.72)$$

where  $\hat{F}_{t_o}$  is the initial value of compression on the boundary. The material constants are obtained from Paul and Ebra-Lima [75] and the previous section, and the non-dimensional constants are calculated to

$$\alpha_1 = 100.151, \quad \alpha_2 = 0.5553. \quad (4.73)$$

Let  $U_i^l$  be  $\hat{f}'$  at  $\hat{t} = t_l$  and  $\hat{Z} = Z_i$ . Then, the equation becomes

$$\hat{g}_1 U'' + \hat{g}_2 U' + \hat{g}_3 \dot{U} = 0. \quad (4.74)$$

Using a central finite difference scheme

$$[\dot{U}]_i^l = \frac{U_i^l - U_i^{l-1}}{\Delta t} \quad (4.75)$$

$$[U']_i^l = \frac{1}{2} \left[ \frac{U_{i+1}^l - U_{i-1}^l}{2\Delta Z} + \frac{U_{i+1}^{l-1} - U_{i-1}^{l-1}}{2\Delta Z} \right] \quad (4.76)$$

$$[U'']_i^l = \frac{1}{2} \left[ \frac{U_{i+1}^l - 2U_i^l + U_{i-1}^l}{(\Delta Z)^2} + \frac{U_{i+1}^{l-1} - 2U_i^{l-1} + U_{i-1}^{l-1}}{(\Delta Z)^2} \right] \quad (4.77)$$

The discretized equation is

$$M_{i+1} U_{i+1}^l + M_i U_i^l + M_{i-1} U_{i-1}^l = B_i \quad (4.78)$$

where

$$M_{i+1} = \frac{\hat{g}_1}{2\Delta Z^2} + \frac{\hat{g}_2}{4\Delta Z} \quad (4.79)$$

$$M_i = -\frac{\hat{g}_1}{2\Delta Z^2} + \frac{\hat{g}_3}{\Delta t} \quad (4.80)$$

$$M_{i-1} = \frac{\hat{g}_1}{2\Delta Z^2} - \frac{\hat{g}_2}{4\Delta Z} \quad (4.81)$$

$$B_i = -\hat{g}_1 \left( \frac{U_{i+1}^{l-1} - 2U_i^{l-1} + U_{i-1}^{l-1}}{2\Delta Z^2} \right) - \hat{g}_2 \left( \frac{U_{i+1}^{l-1} - U_{i-1}^{l-1}}{x\Delta Z} \right) + \hat{g}_3 \left( \frac{U_i^{l-1}}{\Delta t} \right) \quad (4.82)$$

The non-linear equation (4.78) is solved iteratively. An initial guess for  $\mathbf{U}^{l(0)}$  is made. Then, values of  $\hat{g}_1(\mathbf{U}^{l(0)})$ ,  $\hat{g}_2(\mathbf{U}^{l(0)})$ ,  $\hat{g}_3(\mathbf{U}^{l(0)})$ ,  $B(\mathbf{U}^{l(0)})$  and  $\mathbf{M}(\hat{g}_1, \hat{g}_2, \hat{g}_3)$  are calculated and  $\mathbf{U}^{l(1)}$  is obtained by solving (4.78). Again, using  $\mathbf{U}^{l(1)}$  and solving (4.78),  $\mathbf{U}^{l(2)}$  is obtained. In such a way, iteration is continued until the  $k^{th}$  value  $\mathbf{U}^{l(k)}$  satisfies  $\sum_i |U_i^{l(k)} - U_i^{l(k-1)}| < \text{Tol}$ . The surface of the swollen polymer, which is initially in the ‘free swelling’ state, is subjected to a traction given by (while the fluid diffuses in and out freely)

$$\hat{F}_t = \begin{cases} 0 & t < 0 \\ 0.1 & t \geq 0 \end{cases}$$

Figure 17 shows that the volume fraction of solid near the surface decreases first. The volume fraction of solid inside also decreases gradually and finally the system goes to an equilibrium state and the volume fraction of solid becomes constant everywhere. Figure 18 shows the result of the numerical simulation when the load on the surface is released, the swollen polymer absorbs the surrounding fluid and regains the ‘free swelling’ shape. Figure 19 shows the result of numerical calculations of predicting the height change on releasing from different initial compression states.

In Figures 20 and 21, the change in volume fraction at  $Z = 0$  under cyclic loading is plotted. The hysteresis on the total height change due to cyclic load is also shown in Figure 22. If we assume that the area plotted by one cyclic response in Figure 23

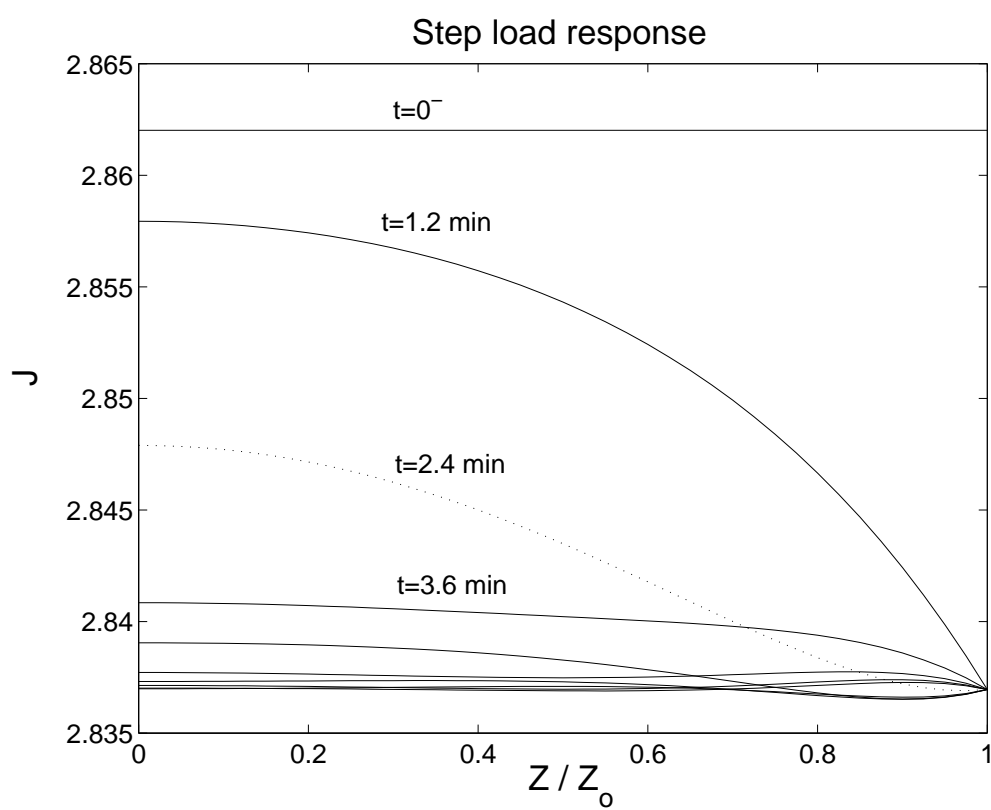


Fig. 17. Volume change of the swollen polymer for the Step load 0.1

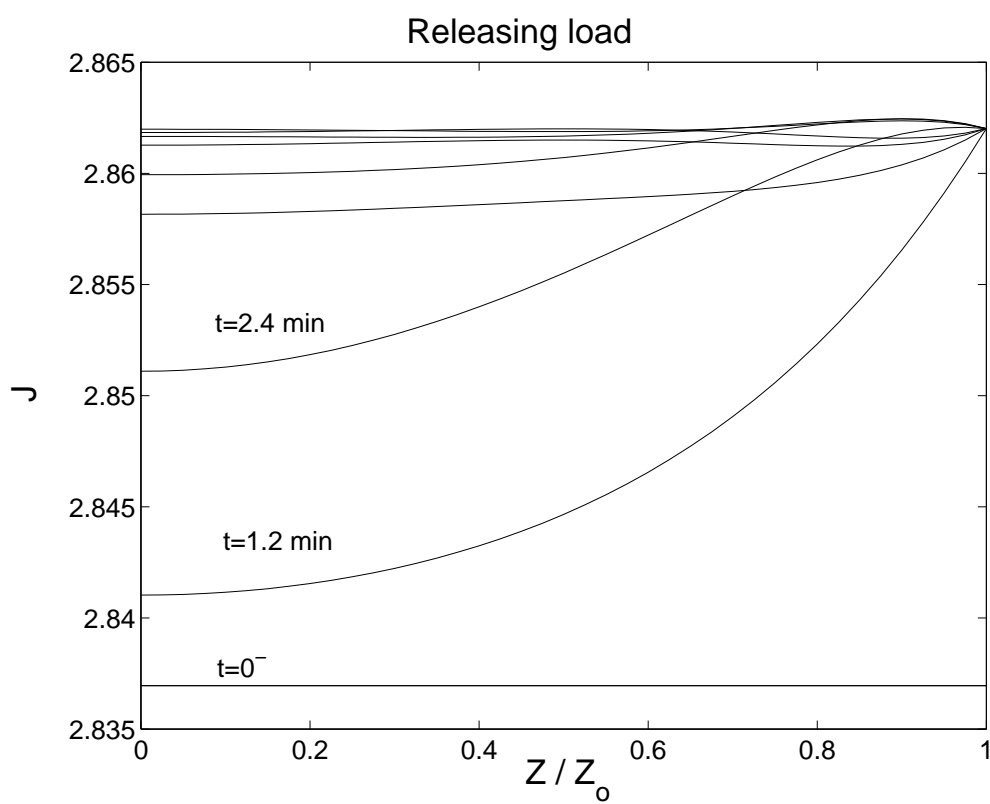


Fig. 18. Volume change of the swollen polymer at release of the load from 0.1 to 0

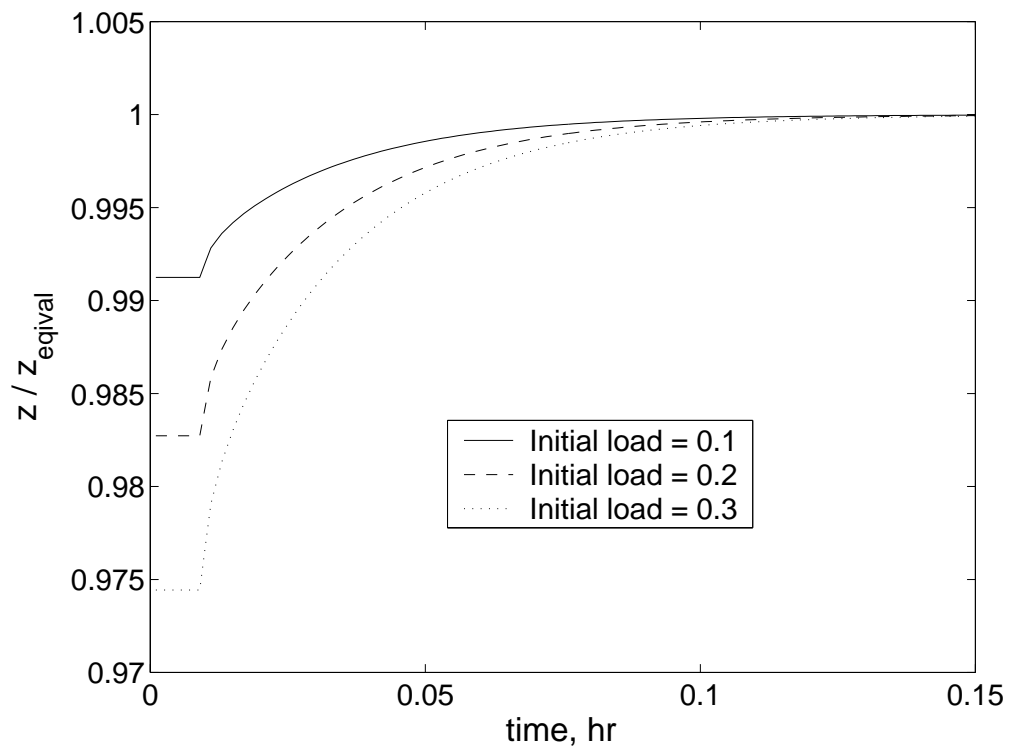


Fig. 19. The height change due to release of supplying load from 0.1, 0.2 and 0.3 to 0



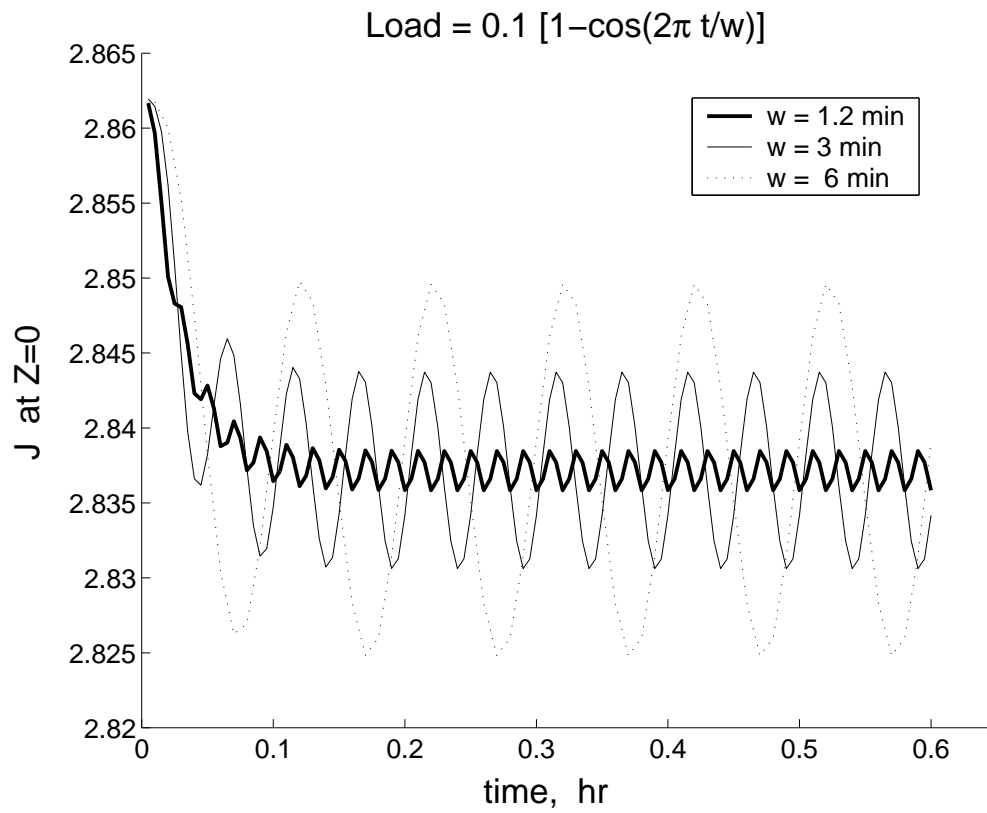


Fig. 20. Volume change at  $Z=0$  under cyclic loading  $F = 0.1 \times (1 - \cos(2\pi t/w))$ . Sharp peaks are shown up because of time steps of computation.

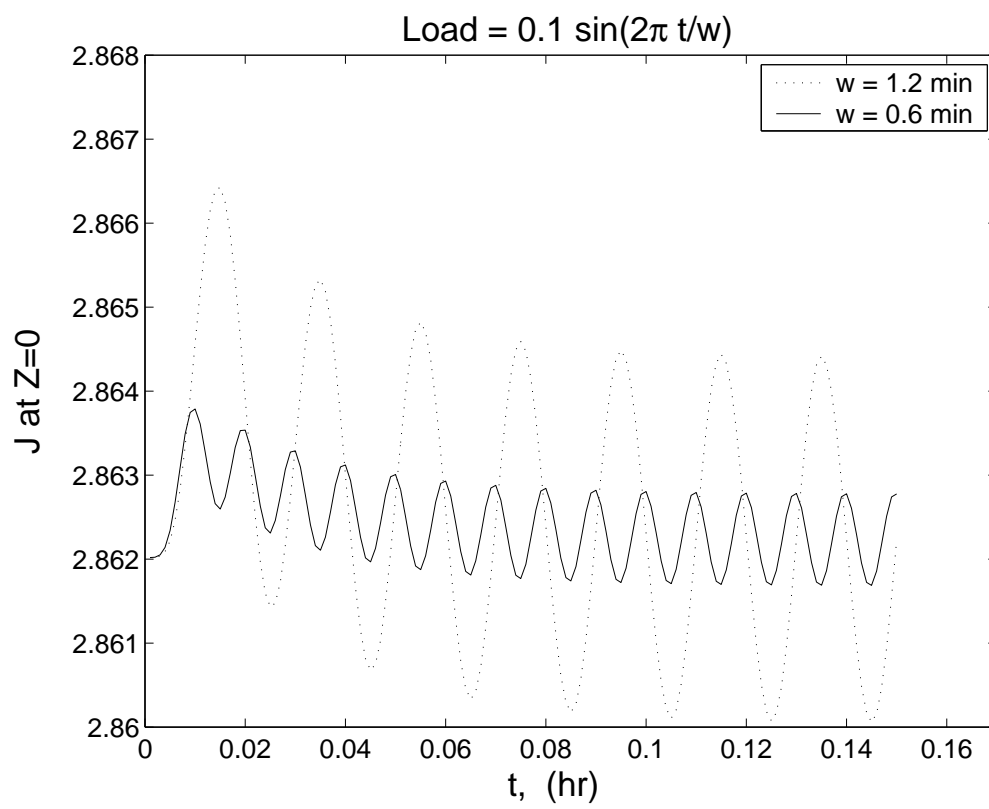


Fig. 21. Volume change at  $Z=0$  under cyclic loading  $F = -0.1 \times \sin(2\pi t/w)$

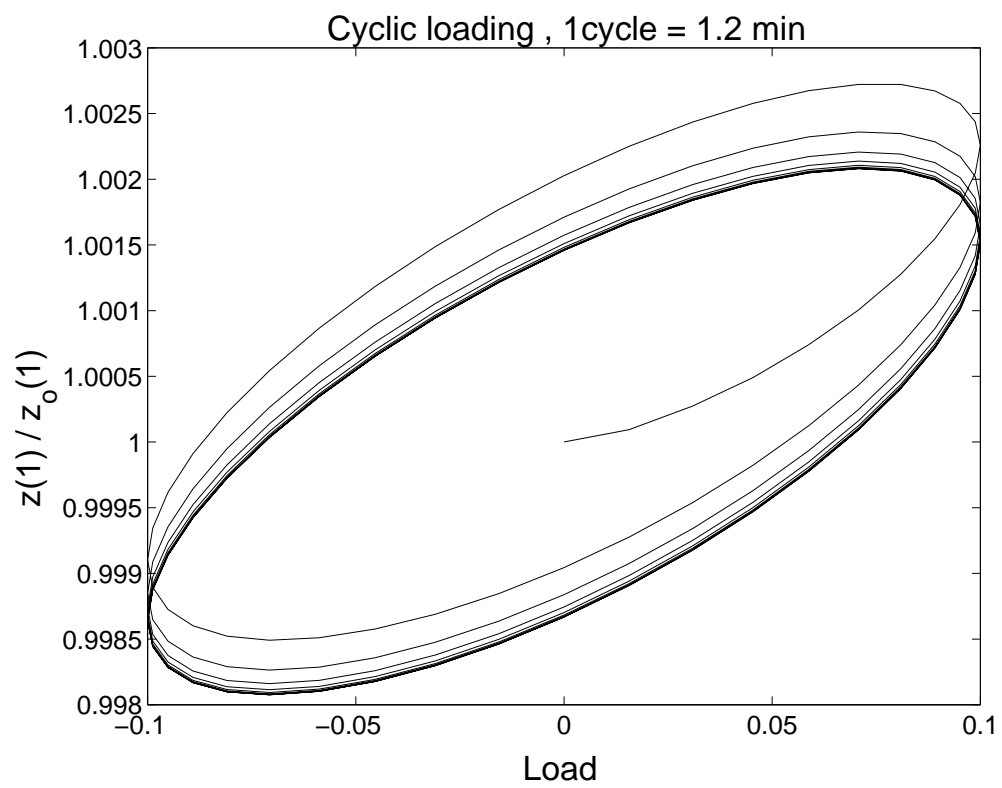


Fig. 22. Hysteresis of the deformation under cyclic loading  $F = -0.1 \times \sin(2\pi t/w)$

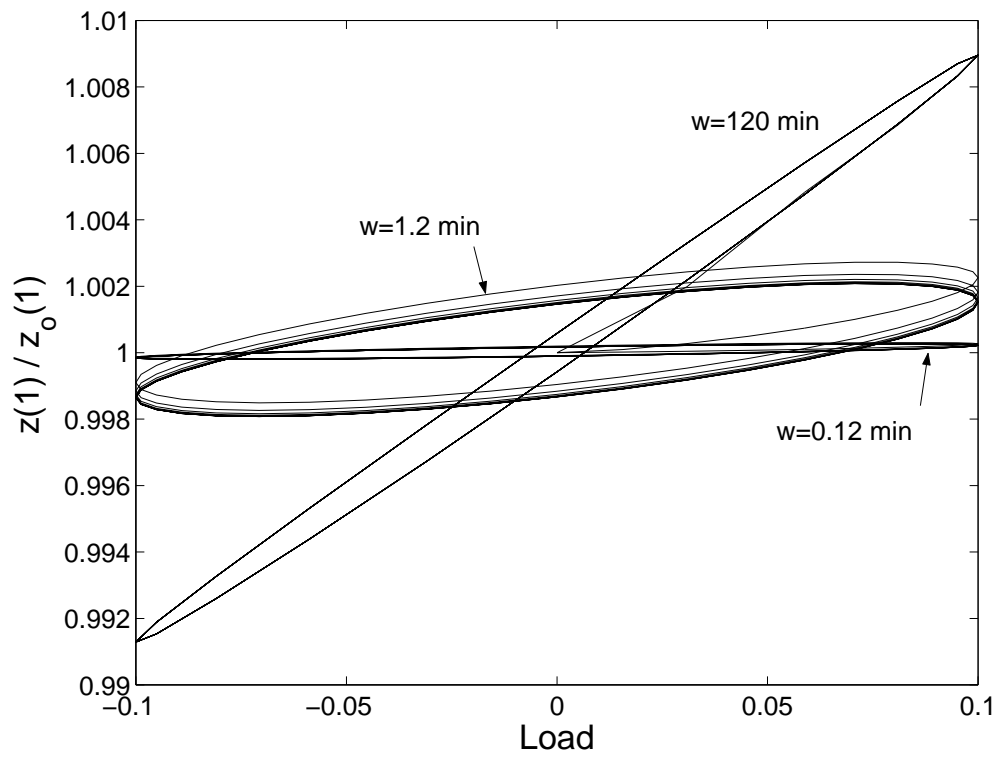


Fig. 23. Hysteresis of the deformation under cyclic loading  $F = -0.1 \times \sin(2\pi t/w)$  for different values of  $w$

represents the loss of work, the cyclic load with  $\omega = 1.2$  min has larger value of the loss of work for one cycle than  $\omega = 0.12$  min and  $\omega = 120$  min. Of course, at the high frequency load, the inertial effect becomes large and we cannot ignore it. These numerical results show the hysteresis behavior of swollen polymer for time dependent load.

#### E. Conclusion

We developed a model for the swollen polymer in the presence of mass flux. When the system is in equilibrium, we find the model is identical to the Flory-Huggins equations and for the system in the presence of mass flux the governing equations are basically the same as those of mixture theory. Assuming specific forms of the Helmholtz potential and the rate of dissipation function, we obtained equations and boundary conditions and found that the numerical results agreed with experimental data very well for the diffusion of organic liquids through pure gum rubber sheet. Also the hysteresis behavior of swollen polymer was studied under time dependent loads.

## CHAPTER V

## OSMOTIC PRESSURE IN A SOLUTION

As we presented in the literature review, the concept of osmotic pressure has been used to explain the swelling behavior of ionic polymers and discussed by many researchers such as Flory [33], Katchalsky and Michaeli [40] and Ogawa *et al.* [41]. So, before we directly extend the model presented in chapter III and IV to swollen ionic polymers, we present the idea of osmotic pressure and, using the variational procedure and the limiting procedure presented in chapter III and a specific form of Helmholtz free energy, we derive the expression for osmotic pressure.

## A. Osmosis and osmotic pressure

Generally, *Osmosis* is the phenomenon of solution flow through a semi-permeable membrane that blocks the transport of salts or other solutes through it. Osmosis is of fundamental importance in biological system. It is applied to water purification and desalination, waste material treatment, and many other chemical and biochemical processes.

Osmosis can be demonstrated by a simple experiment. Consider a beaker (Figure 24) which contains pure water and a semipermeable membrane enclosing component 'B' which cannot pass through the membrane. Water can penetrate through the membrane freely. If, initially, only 'B' is present inside the membrane, the surrounding water will diffuse inside through the membrane and will soon reach its limit due to the pressure produced by the water. Equilibrium exists under these condition and pressure is exerted on the inside of the membrane. The pressure exerted on the membrane is called *osmotic pressure* (van't Hoff [87]).

On the basis of the analogy between the solute particles and gases, van't Hoff

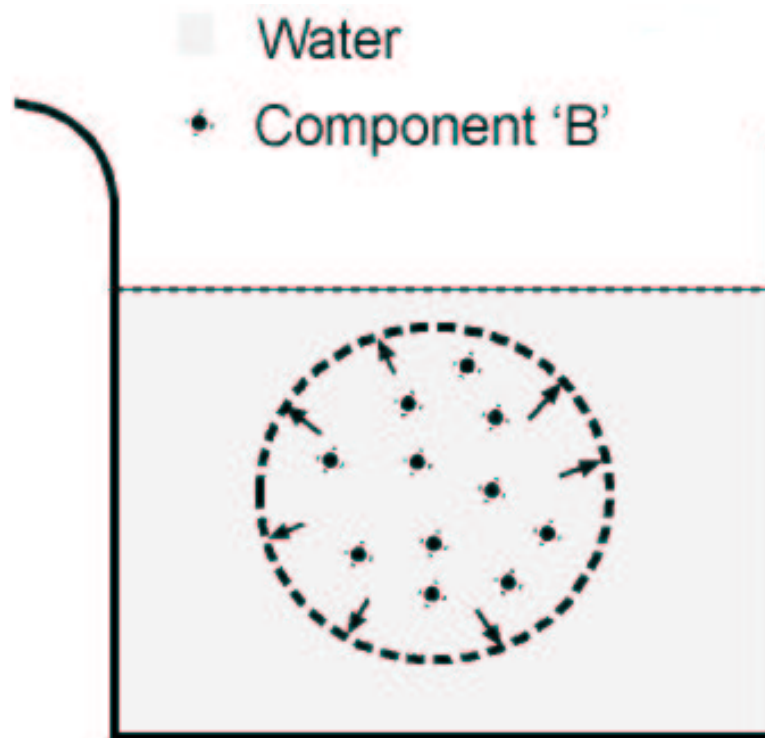


Fig. 24. Schematic view of osmosis

[87] suggested a formula for the osmotic pressure  $\pi$  (now, known as the van't Hoff formula) as

$$\pi = CRT \quad (5.1)$$

where  $C$  is the molar solute concentration. Since the osmotic pressure is generated by collisions of the molecules of 'B' against the membrane, if we assume that the velocity of the free molecules of 'B' in the solution is the same as in a pure gas state, the osmotic pressure is the same as the pressure of gas which contain the same number of moles of the gas 'B'.

Although other theoretical equations for osmotic pressure are suggested, in dilute solution, their results approach the result of van't Hoff equation (5.1) (see Moore [88]). Thus, we will consider (5.1) as the general equation for osmotic pressure.

In the next section, we derive osmotic pressure utilizing the method introduced in Chapter III and using a special form of Helmholtz potential.

#### B. A specific Helmholtz potential and a derivation of osmotic pressure

In Figure 24 the component 'B' is homogeneously distributed inside the membrane (region  $\Omega_1$ ) and the average velocity is  $\mathbf{v}_B$ . The conservation equation for the molar concentration of 'B' is given by

$$\frac{\partial C_B}{\partial t} + \text{div}(C_B \mathbf{v}_B) = 0. \quad \text{in } \Omega_1 \quad (5.2)$$

The mass conservation equation for water in  $\Omega_1$  is

$$\frac{\partial \rho}{\partial t} + \text{div}(\rho \mathbf{v}_B) + \text{div}(\rho \mathbf{v}_{S-B}) = 0 \quad \text{in } \Omega_1 \quad (5.3)$$

where  $\rho$  is the density of the solution and  $\mathbf{v}_{S-B}$  is the relative velocity of the water with respect to  $\mathbf{v}_B$ . The mass conservation equation for the solution outside the



membrane (region  $\Omega_2$ ) is

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{v}_S) = 0 \quad \text{in } \Omega_2 \quad (5.4)$$

The Helmholtz free energy of the solution in  $\Omega_1$  and  $\Omega_2$ , called  $\psi_1$  and  $\psi_2$  respectively, are assumed to be of the form

$$\psi_1 = \hat{\psi}_1(C_B, \rho), \quad \psi_2 = \hat{\psi}_2(\rho) \quad (5.5)$$

Under the assumption that the variation of the total Helmholtz potential of the system  $\Psi$  is equal to the variation of work done on the system  $W$  at equilibrium, we can write the equilibrium condition as

$$\delta\Psi - \delta W = 0. \quad (5.6)$$

When the pressure acting on  $\Gamma_1$  due to the membrane tension is  $P_m$  and the hydrostatic pressure in  $\Omega_2$  is  $P_\infty$ , each term of (5.6) can be rewritten as

$$\delta\Psi = \int_{\Omega_1} \delta\psi_1 dV + \int_{\Omega_2} \delta\psi_2 dV + \int_{\Gamma_1} (\psi_1 - \psi_2) \delta \mathbf{u}_B \cdot \mathbf{n}_1 dA + \int_{\Gamma_2} \psi_2 \delta \mathbf{u}_S \cdot \mathbf{n}_2 dA \quad (5.7)$$

$$\begin{aligned} \delta W = & \int_{\Omega_1} -\mathbf{b} \cdot \delta(\mathbf{u}_B + \mathbf{u}_{S-B}) dV + \int_{\Omega_2} -\mathbf{b} \cdot \delta \mathbf{u}_S dV \\ & - \int_{\Gamma_1} P_m \mathbf{u}_B \cdot \mathbf{n}_1 dA - \int_{\Gamma_2} P_\infty \mathbf{u}_S \cdot \mathbf{n}_2 dA. \end{aligned} \quad (5.8)$$

where  $\mathbf{b}$  is the body force.

Using the chain-rule and the conservation equations, each integrand can be ex-

panded as

$$\begin{aligned}\delta\psi_1 &= \frac{\partial\psi_1}{\partial C_B}\delta C_B + \frac{\partial\psi_1}{\partial\rho}\delta\rho \\ &= -\frac{\partial\psi_1}{\partial C_B}\operatorname{div}(C_B\mathbf{u}_B) - \frac{\partial\psi_1}{\partial\rho}(\operatorname{div}(\rho\mathbf{u}_B) + \operatorname{div}(\rho\mathbf{u}_{S-B}))\end{aligned}\quad (5.9)$$

$$\begin{aligned}\delta\psi_2 &= \frac{\partial\psi_2}{\partial\rho}\delta\rho \\ &= -\frac{\partial\psi_2}{\partial\rho}\operatorname{div}(\rho\mathbf{u}_S).\end{aligned}\quad (5.10)$$

Substituting (5.9) and (5.10) into (5.7) gives

$$\begin{aligned}\delta\Psi &= \int_{\Omega_1} \left[ \operatorname{grad}\left(-\psi_1 + \rho\frac{\partial\psi_1}{\partial\rho} + C_B\frac{\partial\psi_1}{\partial C_B}\right) \cdot \mathbf{u}_B + \rho \operatorname{grad}\left(\frac{\partial\psi_1}{\partial\rho}\right) \cdot \mathbf{u}_{S-B} \right] dV \\ &+ \int_{\Omega_2} \operatorname{grad}\left(-\psi_2 + \rho\frac{\partial\psi_2}{\partial\rho}\right) \cdot \mathbf{u}_S dV \\ &+ \int_{\Gamma_1} \left[ \left(\psi_1 - \rho\frac{\partial\psi_1}{\partial\rho} - C_B\frac{\partial\psi_1}{\partial C_B} - \psi_2 + \rho\frac{\partial\psi_2}{\partial\rho}\right)\mathbf{u}_B \right. \\ &\quad \left. + \left(\rho\frac{\partial\psi_2}{\partial\rho} - \rho\frac{\partial\psi_1}{\partial\rho}\right)\mathbf{u}_{S-B} \right] \cdot \mathbf{n}_1 dA \\ &+ \int_{\Gamma_2} \left(\psi_2 - \rho\frac{\partial\psi_2}{\partial\rho}\right) \cdot \mathbf{n}_2 dA\end{aligned}\quad (5.11)$$

It follows from (5.6), substituting  $\mathbf{b} = -\rho g \mathbf{k}$ , that

$$\operatorname{grad}\left(-\psi_1 + \rho\frac{\partial\psi_1}{\partial\rho} + C_B\frac{\partial\psi_1}{\partial C_B}\right) = -\rho g \mathbf{k} \quad \text{in } \Omega_1 \quad (5.12)$$

$$\rho \operatorname{grad}\left(\frac{\partial\psi_1}{\partial\rho}\right) = -\rho g \mathbf{k} \quad \text{in } \Omega_1 \quad (5.13)$$

$$\operatorname{grad}\left(-\psi_2 + \rho\frac{\partial\psi_2}{\partial\rho}\right) = -\rho g \mathbf{k} \quad \text{in } \Omega_2. \quad (5.14)$$

with boundary conditions

$$\psi_1 - \rho\frac{\partial\psi_1}{\partial\rho} - C_B\frac{\partial\psi_1}{\partial C_B} = \psi_2 - \rho\frac{\partial\psi_2}{\partial\rho} - P_m \quad \text{on } \Gamma_1 \quad (5.15)$$

$$\rho\frac{\partial\psi_1}{\partial\rho} = \rho\frac{\partial\psi_2}{\partial\rho} \quad \text{on } \Gamma_1 \quad (5.16)$$

$$\psi_2 - \rho\frac{\partial\psi_2}{\partial\rho} = -P_\infty \quad \text{on } \Gamma_2 \quad (5.17)$$

As discussed in chapter III, now, we apply the incompressibility constraint on the fluid as a limit process, i.e.,  $\rho = \phi + \rho_o$  and  $\phi \rightarrow 0$  in the limit. Then  $\mu_1 = \partial\psi_1/\partial\rho$  and  $\mu_2 = \partial\psi_2/\partial\rho$  become arbitrary and finite in the limit. The Helmholtz free energy become functions of molar concentrations of components only, i.e.,  $\psi_1 = \tilde{\psi}_1(C_B)$  and  $\psi_2 = \text{constant}$ .

The specific Helmholtz free energy is assumed as

$$\tilde{\psi}_1(C_B) = RTC_B \ln \frac{C_B}{C_B^o} + \psi_2 \quad (5.18)$$

Substituting the specific Helmholtz free energy (5.18), and applying the limit process, the equations (5.12–5.14) reduce to

$$\text{grad}(\rho_o\mu_1 + RTC_B) = -\rho_o g \mathbf{k} \quad \text{in } \Omega_1 \quad (5.19)$$

$$\text{grad}(\rho_o\mu_1) = -\rho_o g \mathbf{k} \quad \text{in } \Omega_1 \quad (5.20)$$

$$\text{grad}(\rho_o\mu_2) = -\rho_o g \mathbf{k} \quad \text{in } \Omega_2 \quad (5.21)$$

and boundary conditions (5.15), (5.16) and (5.17) reduce to

$$-\rho_o\mu_1 - RTC_B = -\rho_o\mu_2 - P_m \quad \text{on } \Gamma_1 \quad (5.22)$$

$$\rho_o\mu_1 = \rho_o\mu_2 \quad \text{on } \Gamma_1 \quad (5.23)$$

$$\psi_2 - \rho_o\mu_2 = -P_\infty \quad \text{on } \Gamma_2 \quad (5.24)$$

Solving (5.21) with boundary condition (5.24) gives

$$\psi_2 - \rho_o\mu_2 = \rho_o g z + c = -P_\infty. \quad (5.25)$$

Let  $P_\infty|_{(z=h)} = P_h$ , then

$$\mu_2 = \frac{\psi_2 + P_h - \rho_o(z - h)}{\rho_o}. \quad (5.26)$$

Solving (5.19) and (5.20) with (5.22) and (5.23) gives

$$P_m = RTC_B \tag{5.27}$$

which gives the osmotic pressure.

In this section, we obtained the van't Hoff formula for the osmotic pressure by assuming a specific form for the Helmholtz potential (5.18).

## CHAPTER VI

MODELING OF THE SWELLING BEHAVIOR OF IONIC POLYMERS IN THE  
PRESENCE OF MASS FLUX AND CHEMICAL REACTIONS

In this chapter we develop and investigate a model for the mechanical behavior of ionic polymers in the presence of mass flux through the body and electro-chemical changes in the environment. The environmental stimulus is the pH of the solution and the ionic polymer will be treated as a pH-sensitive polymer.

In order to account for chemical reaction in our modeling presented in chapter IV, we include molar concentrations of ionizable pendant groups and ions in solution as state variables of the swollen solid. Unlike multi-phasic approaches, e.g. triphasic theory by Lai *et al.* [69], we do not consider the ionic group as a separate phase, but we simply treat them as properties of the swollen solid, so that concentrations of immobile ionizable groups change by their dissociation and the deformation of the network polymer, and concentrations of mobile ion groups change by chemical reactions and mass flux through the swollen solid. We assume that the individual mobile ion cannot move without mass flux, i.e., we do not allow interdiffusion of each ion, although such an extension is possible with multiple mass flux terms. We follow the same thermodynamic frame work which we presented in chapter III and IV for modeling of swollen polymers and extend it to include a chemical reaction.

Before we develop a model for ionic polymers, we briefly review general concepts in chemistry relating to this work.

## A. Basic concepts of chemical reactions in solutions

### 1. Chemical reactions and chemical equilibrium

Let us consider a closed system containing  $n$  components ( $\alpha = 1, \dots, n$ ) and a simple reaction between them. In a closed system variations in mass of the individual constituents result from the chemical reaction. Thus, the change of mass  $m_\alpha$  of constituent  $\alpha$  can be written as

$$\Delta m_\alpha = s_\alpha M_\alpha \Delta r \quad (6.1)$$

where  $M_\alpha$  is the molar mass of constituent  $\alpha$  and  $s_\alpha$  is its stoichiometric coefficient in the chemical reaction. This coefficient  $s_\alpha$  is positive when  $\alpha$  is placed in the product side (the right hand side of a chemical reaction equation) and negative when placed on the reactant side (the left hand side of the reaction equation).  $r$  is the degree of advancement or extent of reaction introduced by De Donder [68] and  $\Delta r$  is the change in extent of reaction. The rate of chemical reaction is denoted by  $\dot{r}$ . The change in the number of moles of constituent  $\alpha$  is given by

$$\Delta C_\alpha = s_\alpha \Delta r. \quad (6.2)$$

As we mentioned in chapter III, for closed systems, at constant temperature and constant volume, the Helmholtz free energy  $\psi$  changes when irreversible chemical reaction occur and remains constant otherwise. Under these later conditions, the variation of the Helmholtz free energy can be written as

$$\delta\psi = \left( \sum_{\alpha=1}^n \frac{\partial\psi}{\partial C_\alpha} \right)_{\theta=\theta_o, V=V_o} \delta C_\alpha = \sum_{\alpha=1}^n s_\alpha \left( \frac{\partial\psi}{\partial C_\alpha} \right)_{\theta=\theta_o, V=V_o} \delta r \quad (6.3)$$

De Donder also introduced the *affinity*  $A$  as the driving force for the reaction of the

system and it can be written as,

$$A = - \sum_{\alpha=1}^n s_{\alpha} \left( \frac{\partial \psi}{\partial C_{\alpha}} \right)_{\theta=\theta_o, V=V_o} \quad (6.4)$$

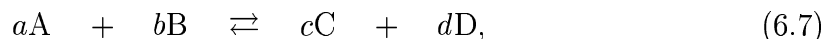
For a chemical reaction the De Donder's inequality gives (De Donder [68])

$$A\dot{r} \geq 0. \quad (6.5)$$

If  $\dot{r}$  is non-zero, the affinity  $A$  should be non-zero. Conditions for equilibrium in a chemical reaction are (see Prigogine and Defay [89])

$$A = 0 \quad \text{and} \quad \dot{r} = 0 \quad (6.6)$$

In a chemical system, equilibrium state may involve phase transformation or chemical reaction. In a chemical reaction, in order to describe equilibrium, the equilibrium constant is used. For a general chemical reaction



Concentration of reactants,  $C_A$  and  $C_B$ , and concentrations of products,  $C_C$  and  $C_D$ , are related by the expression

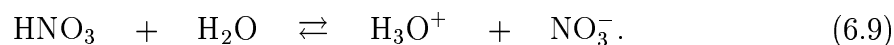
$$K = \frac{C_C^c C_D^d}{C_A^a C_B^b} \quad (6.8)$$

where  $K$  is the equilibrium constant.

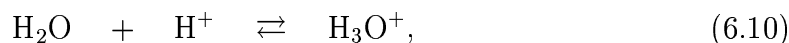
## 2. Acid and base solutions

The  $H^+$  ion is a proton and pure water contains  $10^{-7}$  mole/liter of  $H^+$  ions at  $25^{\circ}C$ .  $H^+$  ion is a tiny particle (less than 0.1 pm) with highly concentrated charge in water and, due to its attraction to the water molecule, the proton exists only associated with the water molecule as a hydrated proton,  $H_3O^+$ . In 1923 Brønsted and Lowry

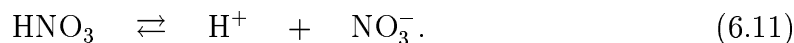
independently suggested a new concept of acid and base behavior. They proposed that an acid is any substance that can donate  $H^+$  to any other substance, and a base is a substance that can accept the proton from any other substance. As an example of an acid, there is nitric acid,  $HNO_3$ . Consider



Combining this equation with the hydration of proton



the reaction equation can be written as



Strong (Brønsted) acids leads to larger concentrations of  $H_3O^+$  than  $10^{-7}$  moles per liter. To compare acid and base strengths quantitatively, we use the pH value of a aqueous solution. pH is defined as the negative of the base-10 logarithm(log) of the hydronium( $H_3O^+$ ) ion concentration, i.e.,

$$pH = -\log C_{H_3O^+}. \quad (6.12)$$

In pure water, the hydronium( $H_3O^+$ ) and hydroxide ( $OH^-$ ) ion concentration are both  $1.0 \times 10^{-7}$  M/liter, so that  $pH=7$ .

### 3. Reactions in ionic solutions

We know that salts dissociate themselves into ions in water. Many properties of ionic solutions depend on electrostatic interactions between ionic charges. The behavior of these ionic solution is no longer governed by ideal equations such as the van't Hoff formula for osmotic pressure (5.1) and the chemical equilibrium equation (6.8).

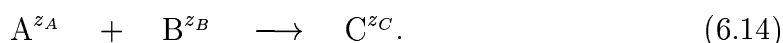


At the beginning of this century G.N. Lewis suggested that, in the osmotic pressure equation (5.1) and the chemical equilibrium equation (6.8), the molar concentrations should be replaced by the *activities* [90]. The activity  $a_A$  of a component 'A' is given by the simple relationship

$$a_A = \gamma_A C_A \quad (6.13)$$

where  $\gamma_A$  is the activity coefficient and  $C_A$  is the molar concentration of the component 'A'. The activity coefficient is a correction factor for non-ideal behavior. In dilute and non-ionic solutions it approaches unity and the activity is identical to the molar concentration.

Debye and Hückel assumed that strong electrolytes are completely dissociated into ions in a solution and derived an electrostatic theory for the dilute solution. They deduced from statistical procedure that the activity coefficient which represents the deviations from ideal behavior is a function of ionic strength. To elaborate, let us consider a dilute solution of component 'A', 'B', and 'C' and their ionic association equation is given by



where  $z_i$  is the charge number of the  $i^{th}$  component and  $z_C = z_A + z_B$ . When the reaction is considered in equilibrium, the equilibrium constant is given by

$$K = \frac{a_C}{a_A a_B} = \frac{\gamma_C}{\gamma_A \gamma_B} \frac{C_C}{C_A C_B} \quad (6.15)$$

In a dilute solution, the activity coefficient terms can be estimated from the Debye-Hückel theory by the relation

$$\log \frac{\gamma_C}{\gamma_A \gamma_B} = \alpha(2z_A z_B) \sqrt{I} = -\alpha(z_A^2 + z_B^2 - z_C^2) \sqrt{I} \quad (6.16)$$

where the ionic strength  $I$  is defined by (see Moore [88])

$$I = \frac{1}{2} \sum_i z_i^2 C_i. \quad (6.17)$$

where the summation is taken over all the different ions in the solution and the constant  $\alpha$  is 0.509.

Substituting (6.16) into (6.15), the equilibrium constant for the reaction results in

$$\ln K = \ln \left( \frac{C_C}{C_A C_B} \right) - \alpha (2z_A z_B) \sqrt{I} \quad (6.18)$$

## B. Preliminaries

Having developed the ideas of reaction rates and activity coefficients, let us consider the system configuration shown in Figure 6 in chapter IV. A swollen pH-sensitive polymer and surrounding ionic solution occupy the regions  $\Omega_m$  and  $\Omega_f$ , respectively. The motion of the swollen body measured from a reference configuration  $\kappa_o$ , the displacement and the deformation gradient of the swollen body are given respectively by

$$\mathbf{x}_m = \chi_{\kappa_o}(\mathbf{X}_m, t), \quad \mathbf{u}_m = \mathbf{x}_m - \mathbf{X}_m, \quad \mathbf{F} = \frac{\partial \chi_{\kappa_o}}{\partial \mathbf{X}_m}, \quad (6.19)$$

where  $\mathbf{X}_m$  and  $\mathbf{x}_m$  are the position of a particle in the body in  $\kappa_o$  and  $\kappa_t$  respectively.

The velocity of the swollen solid is given by

$$\mathbf{v} = \left. \frac{\partial \chi_{\kappa_o}}{\partial t} \right|_{\text{fixed } \mathbf{X}}. \quad (6.20)$$

The motion  $\mathbf{x}_f$ , displacement  $\mathbf{u}_f$  and the velocity  $\mathbf{v}_f$  of the surrounding ionic solution are defined in the same way as that of the mixture region. The densities of the swollen pH-sensitive polymer and the surrounding ionic solution at time  $t$  are  $\rho_m$  and  $\rho_f$  respectively, while  $\rho_{m_o}$  and  $\rho_{f_o}$  denote the densities of the swollen body and the

solution in the initial configuration. The conservation of mass gives

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{v}) + \operatorname{div} \mathbf{q} = 0, \quad \text{in } \Omega_m. \quad (6.21)$$

where  $\mathbf{q}$  denotes the mass flux through the swollen solid. The notation  $\partial(\cdot)/\partial t$  represents a time derivative at a fixed location and the notation  $\operatorname{div}(\cdot)$  stands for the divergence operator with respect to the spatial variables. The conservation of mass for the surrounding fluid occupying the region  $\Omega_f$  gives

$$\frac{\partial \rho_f}{\partial t} + \operatorname{div}(\rho_f \mathbf{v}_f) = 0 \quad \text{in } \Omega_f. \quad (6.22)$$

where  $\mathbf{v}_f$  denotes the velocity field of surrounding fluid.

The volume additivity constraint is given by

$$\rho = \rho_{fo} + \frac{\rho_o - \rho_{fo}}{J}. \quad (6.23)$$

We shall need a new variable  $\phi$ , defined as

$$\phi = \rho - \rho_{fo} - \frac{\rho_o - \rho_{fo}}{J}. \quad (6.24)$$

In the volume additivity limit, the variable  $\phi$  goes to zero.

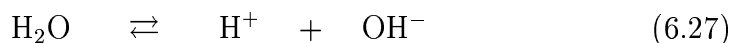
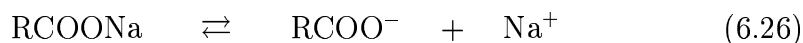
### C. Ionization of an ionizable polymer network

Here, we consider an anionic polymer network containing carboxylic acid in a solutions of NaOH. We assume that NaOH is completely dissociated into  $\text{Na}^+$  and  $\text{OH}^-$  in the solution. Then, there can be reactions and dissociation associated with the reactants

Table IV. Representing variables and their usage

Symbol	Usage
$\alpha$	All chemical components contained in the region
$p$	Immobile components attached as pendant groups of polymers
$m$	Mobile components in the solution
$i$	Ionized components
+	Positively ionized components
-	Negatively ionized components
$k$	$k^{th}$ reaction

RCOOH, RCOO<sup>-</sup>, RCOONa, H<sub>2</sub>O, H<sup>+</sup>, OH<sup>-</sup> and Na<sup>+</sup>, i.e.,



where R represents a polymer backbone group. In order to make the tracing of the various groups simple, different dummy variables are used for the different group of reactants shown in Table IV. The molar concentration per unit volume of the  $\alpha^{th}$  reactant is denoted by  $C_\alpha$  (for example  $C_{\text{H}^+}$  is the molar concentration of H<sup>+</sup> per unit volume). The molar concentration of reactants can be grouped into concentration of

pendant, mobile, ionized, positive and negative groups, i.e.,

$$C_{\alpha} = C_{\text{RCOOH}}, C_{\text{RCOO}^{-}}, C_{\text{RCOONa}}, C_{\text{H}^{+}}, C_{\text{OH}^{-}}, C_{\text{Na}^{+}} \quad (6.28)$$

$$C_{\text{p}} = C_{\text{RCOOH}}, C_{\text{RCOO}^{-}}, C_{\text{RCOONa}} \quad (6.29)$$

$$C_{\text{m}} = C_{\text{H}^{+}}, C_{\text{OH}^{-}}, C_{\text{Na}^{+}} \quad (6.30)$$

$$C_{\text{i}} = C_{\text{RCOO}^{-}}, C_{\text{H}^{+}}, C_{\text{OH}^{-}}, C_{\text{Na}^{+}} \quad (6.31)$$

$$C_{+} = C_{\text{H}^{+}}, C_{\text{Na}^{+}} \quad (6.32)$$

$$C_{-} = C_{\text{RCOO}^{-}}, C_{\text{OH}^{-}} \quad (6.33)$$

For concentrations of reactants in the fluid region, the subscript 'f' is used such as  $C_{\text{fm}}, C_{\text{f+}}, \text{etc.}$

Reactants in the pendent group are attached to the polymer backbone structure, the changes in the molar concentrations  $C_{\text{p}}$  are associated with movement of the swollen body and the reaction rate  $r_k$  ( $r_1, r_2$  and  $r_3$  are extents of reaction of (6.25), (6.26) and (6.27)). In the case of mobile components, they all flow at the same rate as the incoming fluid and their concentrations change with mass flux of the fluid. Conservation equation for the each constituent is given by

$$\frac{\partial C_{\text{p}}}{\partial t} + \text{div}(C_{\text{p}}\mathbf{v}) = \sum_k s_{k,\text{p}}r_k, \quad \text{in } \Omega_s. \quad (6.34)$$

$$\frac{\partial C_{\text{m}}}{\partial t} + \text{div}(C_{\text{m}}\mathbf{v}) + \text{div}\left(\frac{C_{\text{m}}}{\rho_{fo}}\mathbf{q}\right) = \sum_k s_{k,\text{m}}r_k, \quad \text{in } \Omega_s. \quad (6.35)$$

where  $s_{k,\alpha}$  is a stoichiometric number of reactant  $\alpha$  at  $k^{\text{th}}$  reaction and it is negative when the reactant is on the left hand side of the reaction equation. The total molar concentration of the pendant group is depend upon the change in the volume of the

structure and it can be expressed as

$$\sum_p C_p = \nu c_2 \quad (6.36)$$

where  $c_2$  is the total molar concentration of the pendant group per unit volume in the reference configuration.

In the fluid region, the equation for  $C_{f\alpha}$  is given by

$$\frac{\partial C_{f\alpha}}{\partial t} + \text{div}(C_{f\alpha} \mathbf{v}_f) = 0 \quad \text{in } \Omega_f. \quad (6.37)$$

#### D. Variational procedure for the equilibrium state for an unconstrained ionic polymer

Let us assume that the swollen solid and the surrounding fluid are characterized by specific Helmholtz free energy *per unit current volume* of the swollen solid and the surrounding fluid of the form

$$\psi = \hat{\psi}(\mathbf{F}, \rho, C_p, C_m), \quad \psi_f = \hat{\psi}_f(\rho_f, C_{fm}), \quad (6.38)$$

respectively. Then, the total Helmholtz free energy  $\Psi$  is obtained by integrating the two functions over  $\Omega_s$  and  $\Omega_f$ , giving

$$\Psi = \int_{\Omega_s} \psi dV + \int_{\Omega_f} \psi_f dV. \quad (6.39)$$

At constant temperature, the total Helmholtz free energy of the closed system can be interpreted as the available work (see Callen [76]). When the system is in equilibrium, we assumed that the variation of the total Helmholtz free energy is equal to the work done on the system due to the variation of displacement, i.e.,

$$\delta\Psi = \int_{\Gamma_s} \mathbf{t} \cdot \delta\mathbf{u} dA - \int_{\Gamma_f} P_\infty \mathbf{n}_2 \cdot \delta\mathbf{u}_f dA \quad (6.40)$$

In order to find equilibrium state we need to calculate the variation of the Helmholtz potential  $\delta\Psi$ . A routine calculation leads to

$$\begin{aligned}\delta\Psi &= \int_{\Omega_m} \delta\psi dV + \int_{\Gamma_s} (\psi - \psi_f)\delta\mathbf{u} \cdot \mathbf{n}_1 dA \\ &+ \int_{\Omega_f} \delta\psi_f dV + \int_{\Gamma_f} \psi_f \delta\mathbf{u}_f \cdot \mathbf{n}_2 dA\end{aligned}\quad (6.41)$$

The variational term  $\delta\psi$  is expanded by using the chain-rule and equations (6.21–6.22)

as

$$\begin{aligned}\delta\psi &= \frac{\partial\psi}{\partial\mathbf{F}} \cdot \delta\mathbf{F} + \frac{\partial\psi}{\partial\rho} \delta\rho + \sum_p \frac{\partial\psi}{\partial C_p} \delta C_p + \sum_m \frac{\partial\psi}{\partial C_m} \delta C_m \\ &= \frac{\partial\psi}{\partial\mathbf{F}} \mathbf{F}^T \cdot \text{grad} \delta\mathbf{u} - \frac{\partial\psi}{\partial\mathbf{F}} \cdot \text{grad} \mathbf{F} \delta\mathbf{u} - \frac{\partial\psi}{\partial\rho} [\text{div}(\rho\delta\mathbf{u}) + \text{div}(\delta\mathbf{q})] \\ &\quad - \sum_m \frac{\partial\psi}{\partial C_m} [\text{div}(C_m\delta\mathbf{u}) + \text{div}\left(\frac{C_m}{\rho_{fo}}\delta\mathbf{q}\right) - \sum_k s_{k,m}\delta r_k] \\ &\quad - \sum_p \frac{\partial\psi}{\partial C_p} [\text{div}(C_p\delta\mathbf{u}) - \sum_k s_{k,p}\delta r_k] \\ &= \frac{\partial\psi}{\partial\mathbf{F}} \mathbf{F}^T \cdot \text{grad}\delta\mathbf{u} - \text{grad}\psi \cdot \delta\mathbf{u} - \left[\rho \frac{\partial\psi}{\partial\rho} + \sum_\alpha C_\alpha \frac{\partial\psi}{\partial C_\alpha}\right] \text{div}\delta\mathbf{u} \\ &\quad - \left(\frac{\partial\psi}{\partial\rho}\right) \text{div} \mathbf{q} - \sum_m \left(\frac{\partial\psi}{\partial C_m}\right) \text{div}\left(\frac{C_m}{\rho_{fo}}\delta\mathbf{q}\right) + \sum_k \left(\sum_\alpha s_{k,\alpha} \frac{\partial\psi}{\partial C_\alpha}\right) \delta r_k\end{aligned}\quad (6.42)$$

The variation of Helmholtz free energy in surrounding fluid is expanded as

$$\begin{aligned}\delta\psi_f &= \frac{\partial\psi_f}{\partial\rho_f} \delta\rho_f + \sum_m \frac{\partial\psi_f}{\partial C_{fm}} \delta C_{fm} \\ &= -\text{grad}\psi_f \cdot \delta\mathbf{u}_f - \left(\rho_f \frac{\partial\psi_f}{\partial\rho_f} + \sum_m C_{fm} \frac{\partial\psi_f}{\partial C_{fm}}\right) \text{div}\delta\mathbf{u}_f\end{aligned}\quad (6.43)$$

Substituting (6.42) and (6.43) into (6.41), and using divergence theorem, the variation of total stored energy is obtained as

$$\begin{aligned}
\delta\Psi &= \int_{\Omega_s} \left( \left[ -\operatorname{div}\left(\frac{\partial\psi}{\partial\mathbf{F}}\mathbf{F}^T\right) - \operatorname{grad}\left(\psi - \rho\frac{\partial\psi}{\partial\rho} - \sum_{\alpha} C_{\alpha}\frac{\partial\psi}{\partial C_{\alpha}}\right) \right] \cdot \delta\mathbf{u} \right. \\
&\quad \left. + \left[ \operatorname{grad}\left(\frac{\partial\psi}{\partial\rho}\right) + \sum_m \frac{C_m}{\rho_{fo}} \operatorname{grad}\left(\frac{\partial\psi}{\partial C_m}\right) \right] \cdot \delta\mathbf{q} + \sum_k \left( \sum_{\alpha} s_{k,\alpha} \frac{\partial\psi}{\partial C_{\alpha}} \right) \delta r_k \right) dV \\
&+ \int_{\Omega_f} \left( -\operatorname{grad}\left[\psi_f - \rho_f \frac{\partial\psi_f}{\partial\rho_f} - \sum_m C_{fm} \frac{\partial\psi_f}{\partial C_{fm}}\right] \cdot \delta\mathbf{u}_f \right) dV \tag{6.44} \\
&+ \int_{\Gamma_s} \left( \left[ \mathbf{F}\left(\frac{\partial\psi}{\partial\mathbf{F}}\right)^T + \left(\psi - \rho\frac{\partial\psi}{\partial\rho} - \sum_{\alpha} C_{\alpha}\frac{\partial\psi}{\partial C_{\alpha}}\right)\mathbf{I} \right. \right. \\
&\quad \left. \left. - \left(\psi_f - \rho_f \frac{\partial\psi_f}{\partial\rho_f} - \sum_m C_{fm} \frac{\partial\psi_f}{\partial C_{fm}}\right)\mathbf{I} \right] \delta\mathbf{u} \right. \\
&\quad \left. + \left[ \frac{\partial\psi_f}{\partial\rho_f} - \frac{\partial\psi}{\partial\rho} + \sum_m \left( \frac{C_{fm}}{\rho_{fo}} \frac{\partial\psi_f}{\partial C_{fm}} - \frac{C_m}{\rho_{fo}} \frac{\partial\psi}{\partial C_m} \right) \right] \delta\mathbf{q} \right) \cdot \mathbf{n}_1 dA \\
&+ \int_{\Gamma_f} \left( \left[ \psi_f - \rho_f \frac{\partial\psi_f}{\partial\rho_f} - \sum_m C_{fm} \frac{\partial\psi_f}{\partial C_{fm}} \right] \delta\mathbf{u}_f \right) \cdot \mathbf{n}_2 dA
\end{aligned}$$

then, by the usual procedure of the calculus of variations, we arrive at the differential equations that characterize the equilibrium configuration of the system in the form

$$\operatorname{div}(\hat{\mathbf{T}}) = \mathbf{0} \quad \text{in } \Omega_s \tag{6.45}$$

$$\operatorname{grad}\left(\frac{\partial\psi}{\partial\rho}\right) + \sum_m \frac{C_m}{\rho_{fo}} \operatorname{grad}\left(\frac{\partial\psi}{\partial C_m}\right) = 0 \quad \text{in } \Omega_s \tag{6.46}$$

$$\sum_{\alpha} s_{k,\alpha} \frac{\partial\psi}{\partial C_{\alpha}} = 0 \quad \text{in } \Omega_s \tag{6.47}$$

where

$$\hat{\mathbf{T}} = \frac{\partial\psi}{\partial\mathbf{F}}\mathbf{F}^T + \left(\psi - \rho\frac{\partial\psi}{\partial\rho} - \sum_{\alpha} C_{\alpha}\frac{\partial\psi}{\partial C_{\alpha}}\right)\mathbf{I}, \tag{6.48}$$

together with the natural boundary conditions

$$\hat{\mathbf{T}}\mathbf{n}_1 = \mathbf{t} + \left(\psi_f - \rho_f \frac{\partial\psi_f}{\partial\rho_f} - \sum_m C_{fm} \frac{\partial\psi_f}{\partial C_{fm}}\right)\mathbf{n}_1 \quad \text{on } \Gamma_s \tag{6.49}$$

$$\frac{\partial\psi}{\partial\rho} + \sum_m \frac{C_m}{\rho_{fo}} \frac{\partial\psi}{\partial C_m} = \frac{\partial\psi_f}{\partial\rho_f} + \sum_m \frac{C_{fm}}{\rho_{fo}} \frac{\partial\psi_f}{\partial C_{fm}} \quad \text{on } \Gamma_s \tag{6.50}$$



Here, we should note that this calculus of variation does not give the equilibrium conditions for the concentrations of ions across the boundary, because we did not allow for interdiffusion of each ion. For an ionic solution, the concentration of an ion is not continuous across the interface, which was first explained by Donnan [39]. Donnan assumed that, if there existed no electrostatic potential change for the variation of the  $i^{\text{th}}$  ion, this would lead to the equation of equilibrium  $C_i = C_{fi}$ , but a electrostatical potential change exists for the variation and, therefore, the concentration of the ion is not continuous across the interface. Thus, we assume that each ion satisfies the equilibrium condition so that there is no interdiffusion of each ion across the interface. This equilibrium condition for each ion gives

$$\frac{\partial\psi}{\partial C_i} = \frac{\partial\psi_f}{\partial C_{fi}} \quad \text{on } \Gamma_s. \quad (6.51)$$

When the difference in the electrostatic potentials across the boundary is negligible, the condition (6.51) approaches  $C_i = C_{fi}$ , and this case will be discussed later for the specific problem of our concern.

At constant temperature, the affinity of the  $k^{\text{th}}$  reaction,  $A_k$ , is defined as (see Prigogine [89])

$$A_k = - \sum_{\alpha} s_{k,\alpha} \frac{\partial\psi}{\partial C_{\alpha}}. \quad (6.52)$$

The equation (6.47) expresses the condition for equilibrium of the  $k^{\text{th}}$  reaction and it is

$$A_k = 0. \quad (6.53)$$

In the surrounding fluid region, the field equation is given by

$$\text{grad} \left[ \psi_f - \rho_f \frac{\partial\psi_f}{\partial \rho_f} - \sum_m C_{fm} \frac{\partial\psi_f}{\partial C_{fm}} \right] = 0 \quad \text{in } \Omega_f \quad (6.54)$$

and the natural boundary condition is obtained as

$$\psi_f - \rho_f \frac{\partial \psi_f}{\partial \rho_f} - \sum_m C_{fm} \frac{\partial \psi_f}{\partial C_{fm}} = -P_\infty \quad \text{on } \Gamma_f \quad (6.55)$$

Solving (6.54) with respect to (6.55), we obtain the following equation for the surrounding fluid in the region  $\Omega_f$

$$\psi_f - \rho_f \frac{\partial \psi_f}{\partial \rho_f} - \sum_m C_{fm} \frac{\partial \psi_f}{\partial C_{fm}} = -P_\infty \quad \text{in } \Omega_f \quad (6.56)$$

#### E. The limit of constraints for unconstrained ionic polymers

Here, we utilize the definition of partial chemical potential for mass flux, which is introduced in chapter III,

$$\mu = \frac{\partial \psi}{\partial \rho} \quad (6.57)$$

$$\mu_f = \frac{\partial \psi_f}{\partial \rho_f} \quad (6.58)$$

Until now the volume additivity constraint and the incompressibility constraint on the surrounding fluid have not been imposed. Rather than treat these two conditions as constraints, we shall consider them as limiting cases when the compressibility of the fluid and the volume additivity of the swollen solid tend to zero. Let us rewrite the constitutive equation for the Helmholtz potential in the form

$$\psi = \hat{\psi}(\mathbf{F}, \rho, C_m, C_p) = \psi^*(\mathbf{F}, \phi, C_m, C_p). \quad (6.59)$$

where  $\phi$  is defined in (6.24). Using the chain-rule, (6.57) and (6.48) reduce to

$$\mu = \frac{\partial \psi^*}{\partial \phi} \quad (6.60)$$

$$\hat{\mathbf{T}} = \frac{\partial \psi^*}{\partial \mathbf{F}} \mathbf{F}^T + \left( \psi^* - (\phi + \rho_{fo})\mu - \sum_\alpha C_\alpha \frac{\partial \psi^*}{\partial C_\alpha} \right) \mathbf{I} \quad (6.61)$$

In the limit when  $\phi$  becomes zero, it is revealed that the chemical potential  $\mu$  defined by (6.60) remains finite and is no longer determined from a constitutive equation. Instead it is determined by solving a boundary value problem.  $\mu$  can be expanded in a Taylor series around  $\phi = 0$  as

$$\mu(\phi) = \frac{\partial\psi^*}{\partial\phi}\Big|_{\phi=0} + \frac{\partial^2\psi^*}{\partial\phi^2}\Big|_{\phi=0}\phi + \dots \quad (6.62)$$

where the first term of the right hand side of (6.62) is the finite value of the chemical potential  $\mu(\phi = 0)$ . In the limit,  $\frac{\partial^2\psi^*}{\partial\phi^2}\Big|_{\phi=0} \rightarrow \infty$  and  $\phi \rightarrow 0$  in such a way that their product remains finite. So the sum of the initial finite value of chemical potential and the finite value of the limit yields an arbitrary but finite value for the chemical potential. Also at the limit  $\psi$  becomes zero and  $\psi^*(\mathbf{F}, \phi, C_\alpha)$  becomes a function of  $\mathbf{F}$  and  $C_\alpha = \{C_m, C_p\}$ . This limiting function will be referred as  $\tilde{\psi}(\mathbf{F}, C_\alpha)$ .

A similar argument using the limit of the incompressibility constraint,  $\rho_f = \rho_{fo}$ , of the fluid in  $\Omega_f$  reveals that  $\mu_f$  becomes finite and undetermined. Also  $\rho_f$  becomes a constant  $\rho_{fo}$  and the constitutive function  $\psi_f$  becomes a function of  $C_{fm}$  alone in the limit. The function will be referred as  $\tilde{\psi}_f(C_{fm})$ .

It follows from (6.45), (6.46) and the above limit processes that the equation of system are given by

$$\operatorname{div}(\hat{\mathbf{T}}) = \mathbf{0} \quad \text{in } \Omega_s \quad (6.63)$$

$$\operatorname{grad}\mu + \sum_m \frac{C_m}{\rho_{fo}} \operatorname{grad}\left(\frac{\partial\tilde{\psi}}{\partial C_m}\right) = 0 \quad \text{in } \Omega_s \quad (6.64)$$

$$A_k = 0 \quad \text{in } \Omega_s \quad (6.65)$$

where

$$\hat{\mathbf{T}} = \frac{\partial \tilde{\psi}}{\partial \mathbf{F}} \mathbf{F}^T + (\tilde{\psi} - \rho_{fo} \mu - \sum_{\alpha} C_{\alpha} \frac{\partial \tilde{\psi}}{\partial C_{\alpha}}) \mathbf{I}, \quad (6.66)$$

$$A_k = - \sum_{\alpha} s_{k,\alpha} \frac{\partial \tilde{\psi}}{\partial C_{\alpha}} \quad (6.67)$$

The natural boundary conditions (6.49–6.50), combined with (6.56), reduce to

$$\hat{\mathbf{T}} \mathbf{n}_1 = \mathbf{t} + (\tilde{\psi}_f - \rho_{fo} \mu_f - \sum_m C_{fm} \frac{\partial \tilde{\psi}_f}{\partial C_{fm}}) \mathbf{n}_1 \quad \text{on } \Gamma_s \quad (6.68)$$

$$\mu + \sum_m \frac{C_m}{\rho_{fo}} \frac{\partial \tilde{\psi}}{\partial C_m} = \mu_f + \sum_m \frac{C_{fm}}{\rho_{fo}} \frac{\partial \tilde{\psi}_f}{\partial C_{fm}} \quad \text{on } \Gamma_s \quad (6.69)$$

## F. Dissipative processes

In the previous development in this chapter, the system considered to be in equilibrium. In this section, we will consider the dissipative processes that the ionic polymer is capable of undergoing. For example during the process of swelling, fluid diffusion takes place. Similarly the process of association and dissociation of the ions can also give rise to entropy production. The total rate of dissipation for an isothermal process is defined by

$$\int_{\Gamma_s} \mathbf{t} \cdot \mathbf{v} dA - \int_{\Gamma_f} P_{\infty} \mathbf{n}_2 \cdot \mathbf{v}_f dA - \frac{d\Psi}{dt} := \Sigma. \quad (6.70)$$

The total rate of dissipation of the swollen body can be obtained by manipulation of the above expression as

$$\begin{aligned}
\Sigma_s &= \int_{\Omega_s} \left( \operatorname{div}(\hat{\mathbf{T}}) \cdot \mathbf{v} - \operatorname{grad} \mu \cdot \mathbf{q} - \sum_m \operatorname{grad} \left( \frac{\partial \psi}{\partial C_m} \right) \cdot \left( \frac{C_m}{\rho_{fo}} \mathbf{q} \right) + \sum_k A_k r_k \right) dV \\
&+ \int_{\Gamma_s} \left( - (\hat{\mathbf{T}} - (\psi_f - \sum_m C_{fm} \frac{\partial \psi_f}{\partial C_{fm}} - \rho_f \mu_f) \mathbf{I}) \mathbf{v} \cdot \mathbf{n}_1 + \mathbf{t} \cdot \mathbf{v} \right. \\
&\quad \left. + \left( \mu - \mu_f + \sum_m \left( \frac{C_m}{\rho_{fo}} \frac{\partial \psi}{\partial C_m} - \frac{C_{fm}}{\rho_{fo}} \frac{\partial \psi_f}{\partial C_{fm}} \right) \right) \mathbf{q} \cdot \mathbf{n}_1 \right) dA \\
&:= \int_{\Omega_s} \xi_{(b)} dV + \int_{\Gamma_s} \xi_{(s)} dA \tag{6.71}
\end{aligned}$$

where the bulk rate of specific dissipation  $\xi_{(b)}$  and the surface rate of specific dissipation  $\xi_{(s)}$  are defined for the sake of simplicity.

Here, following the same procedure for dissipative processes presented in chapter IV, we shall postulate constitutive forms for  $\xi_{(b)}$  and  $\xi_{(s)}$ . These forms are chosen to be non-negative and to reflect the dissipation process of the system. We also utilize the variational method based on the assumption of maximum rate of dissipation.

We assume that the boundary of the pH-sensitive hydrogel is saturated so that the surface dissipation vanishes, i.e.,

$$\xi_{(s)} = 0. \tag{6.72}$$

The bulk rate of dissipation is assumed to be a function of the deformation gradient of the swollen body and the flux through it, in the form

$$\xi_{(b)} = \hat{\xi}(\mathbf{F}, \mathbf{q}, C_\alpha, r_k). \tag{6.73}$$

To carry out this maximization subject to (6.73), the auxiliary function  $\tilde{\Sigma}$  is introduced using the technique of Lagrange multiplier, by

$$\tilde{\Sigma}_m := \Sigma_m + \int_{\Omega_m} \lambda (\xi_{(b)} - \hat{\xi}) dV \tag{6.74}$$

where  $\lambda$  is a Lagrange multiplier. Extremizing  $\tilde{\Sigma}_m$  over the set of all kinematically admissible velocity fields and the flux fields, and taking the limit of volume additivity, the field equations are obtained as

$$\operatorname{div}(\hat{\mathbf{T}}) = 0 \quad (6.75)$$

$$\operatorname{grad} \mu + \sum_m \frac{C_m}{\rho_{fo}} \operatorname{grad} \left( \frac{\partial \tilde{\psi}}{\partial C_m} \right) = -\tilde{\lambda} \frac{\partial \hat{\xi}}{\partial \mathbf{q}} \quad (6.76)$$

$$A_k = \tilde{\lambda} \frac{\partial \hat{\xi}}{\partial r_k}, \quad (6.77)$$

where  $\tilde{\lambda} = \lambda/(1 + \lambda)$ . Solving (6.71), (6.75) and (6.76),  $\tilde{\lambda}$  is obtained as

$$\tilde{\lambda} = \frac{\hat{\xi}}{\frac{\partial \hat{\xi}}{\partial \mathbf{q}} \cdot \mathbf{q} + \sum_k \frac{\partial \hat{\xi}}{\partial r_k} r_k} \quad (6.78)$$

Boundary conditions are obtained as

$$\hat{\mathbf{T}} \mathbf{n}_1 = \mathbf{t} + \left( \tilde{\psi}_f - \sum_m C_{fm} \frac{\partial \tilde{\psi}_f}{\partial C_{fm}} - \rho_{fo} \mu_f \right) \mathbf{n}_1 \quad (6.79)$$

$$\mu + \sum_m \frac{C_m}{\rho_{fo}} \frac{\partial \tilde{\psi}}{\partial C_m} = \mu_f + \sum_m \frac{C_{fm}}{\rho_{fo}} \frac{\partial \tilde{\psi}_f}{\partial C_{fm}} \quad (6.80)$$

From the assumption on the boundary (6.72) and (6.56), the indeterminate  $\mu_f$  can be obtained as

$$\mu_f = \frac{1}{\rho_{fo}} \left( P_\infty + \tilde{\psi}_f - \sum_m C_{fm} \frac{\partial \tilde{\psi}_f}{\partial C_{fm}} \right) \quad (6.81)$$

### G. Specific forms of the Helmholtz potential and the rate of dissipation functions

To obtain specific solutions for the system, we need to know the Helmholtz free energy of the system. It may be assumed to be a sum of non-ionic and ionic terms;

$$\tilde{\psi} = \tilde{\psi}_{sw} + \tilde{\psi}_{ion} \quad (6.82)$$

In the case of swollen network polymer without ionization, the Helmholtz free energy of the swollen body can be assumed of the form [see (4.5) in chapter IV]:

$$\tilde{\psi}_{sw} = \frac{\nu\rho_o RT}{2M}(\text{tr}(\mathbf{F}\mathbf{F}^T) - 3 + \ln\nu) + \frac{RT}{V_o} \left( (1-\nu)\ln(1-\nu) - \chi\nu^2 \right) \quad (6.83)$$

where the first term of right hand side of (6.83) is the elastic energy of the polymer network and the second term is the free energy change due to the entropy of mixing. The contribution of the dissociation of the anionic pendant group to the Helmholtz free energy is assumed to consist of two terms one from the entropy change and another from the electrostatic energy:

$$\tilde{\psi}_{ion} = -T\Delta S + \Delta U_{es}. \quad (6.84)$$

In order to find  $\Delta S$ , let us look at a simple statistical method similar to that of Flory [34]. Molecules of water, mobile ions and immobile pendant groups are assumed to be arranged on a three-dimensional lattice of sites (see Figure 25) such that each site may be occupied by one molecule of water, a mobile ion or an immobile pendant group. The pendant groups are attached to the polymer network so that their positions are fixed. If the total number of sites is  $N^t$ , the total number of sites occupied by mobile ions  $\{M1, M2, \dots, Mm\}$  is  $N_m^t = \sum_m N_m = N_{m1} + N_{m2} + \dots + N_{mm}$ , and the total number of sites occupied by pendant groups  $\{P1, P2, \dots, Pp\}$  is  $N_p^t = \sum_p N_p = N_{p1} + N_{p2} + \dots + N_{pp}$ , then the total number of *distinguishable* configurations for the system  $Z$  is the product of the number of distinguishable configurations for mobile ions  $Z_m$  and that for pendant groups  $Z_p$ , i.e.,

$$Z = Z_m Z_p = \left\{ \frac{(N^t - N_p^t)!}{N_{m1}! N_{m2}! \dots N_{mm}! (N^t - N_p^t - N_m^t)!} \right\} \left\{ \frac{N_p^t!}{N_{p1}! N_{p2}! \dots N_{pp}!} \right\}. \quad (6.85)$$

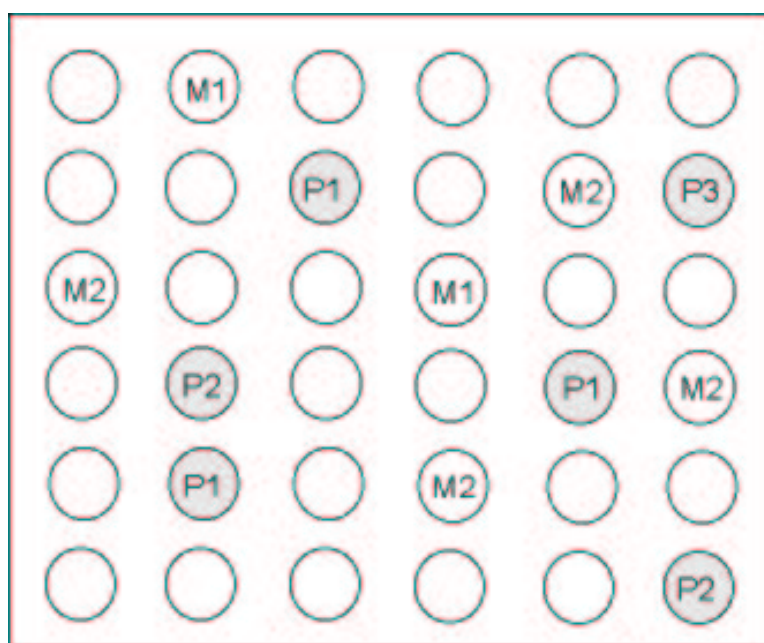


Fig. 25. Schematic representation of lattice model. The circles P1, P2 and P3 represent molecules of P1, P2 and P3 pendant groups. The circles M1 and M2 represent molecules of mobile ions



Using the representation of groups shown in Table IV, (6.85) can be written as

$$Z = \frac{(N^t - N_p^t)! N_p^t!}{N_{\alpha 1}! N_{\alpha 2}! \dots N_{\alpha \alpha}! (N^t - N_p^t - N_m^t)!} \quad (6.86)$$

where the group  $\alpha$  includes both of mobile ions and pendant groups. The configurational entropy per unit volume  $\Delta S$  is obtained from (6.86) by the use of the Boltzman's relation and the Stirling's approximation as

$$\begin{aligned} \Delta S = \frac{k}{V^t} & \left\{ N_p^t \ln \left( \frac{N_p^t}{N^t - N_p^t} \right) - \sum_{\alpha} N_{\alpha} \ln \left( \frac{N_{\alpha}}{N^t - N_p^t} \right) \right. \\ & \left. - (N^t - N_p^t - N_m^t) \ln \left( \frac{N^t - N_p^t - N_m^t}{N^t - N_p^t} \right) \right\} \end{aligned} \quad (6.87)$$

where  $k$  and  $V^t$  are the Boltzman constant and the total volume. When  $N^t \gg N_m^t$  and  $N^t \gg N_p^t$ , the last term in (6.87) goes to zero and its first derivatives with respect to  $N_p^t$  and  $N_m^t$  also go to zero, so that we can ignore the term. Then, (6.87) can reduce to

$$\Delta S = R c_2 \nu \ln \nu_p - R \sum_{\alpha} C_{\alpha} \ln \nu_{\alpha} \quad (6.88)$$

where  $R$  is the gas constant,  $c_2 \nu$  is the molar concentration of total pendant groups ( $c_2 \nu = \sum_p C_p$ ),  $\nu_p$  is the volume fraction of the total pendant groups,  $\nu_{\alpha}$  is the volume fraction of the  $\alpha^{th}$  component. Finally the entropy  $\Delta S$  can be written as

$$\Delta S = R c_2 \nu \ln (V_p c_2 \nu) - R \sum_{\alpha} C_{\alpha} \ln (V_{\alpha} C_{\alpha}) \quad (6.89)$$

where  $V_p$  and  $V_{\alpha}$  are molar volumes of pendant groups and the  $\alpha^{th}$  component.

For the electrostatic component of the free energy  $\Delta U_{es}$ , various models have been developed [91, 92, 93]. Recently, Achilleos *et al.* [94] suggested an electrostatic Helmholtz potential form for a polyelectrolyte due to charging the mobile ions in

terms of ionic strength. Here, we use the following form for  $\Delta U_{es}$

$$\Delta U_{es} = \frac{2RTk_I}{3} I^{3/2}. \quad (6.90)$$

where the ionic strength is defined as  $I = \frac{1}{2} \sum_i (z_i)^2 C_i$  and  $z_i$  is the charge number of  $i^{\text{th}}$  ion. Substitution (6.89) and (6.90) into (6.84) results in

$$\tilde{\psi}_{ion} = RT \left[ \sum_{\alpha} C_{\alpha} \ln \frac{C_{\alpha}}{C_{\alpha}^o} - c_2 \nu \ln \frac{c_2 \nu}{C_p^o} + \frac{2k_I}{3} I^{3/2} \right]. \quad (6.91)$$

where  $C_{\alpha}^o = 1/V_{\alpha}$  and  $C_p^o = 1/V_p$ .

The Helmholtz free energy of the surrounding fluid is given by a function of  $C_{fm}$  alone, in the form

$$\tilde{\psi}_f = RT \left[ \sum_m C_{fm} \ln \frac{C_{fm}}{C_m^o} + \frac{2k_I}{3} I_f^{3/2} \right] \quad (6.92)$$

where  $C_m^o = 1/V_m$  and  $I_f = \frac{1}{2} \sum_i (z_i)^2 C_{fi}$ .

We assume that the rate of dissipation function can be divided into two parts: the rate of dissipation associated with diffusion  $\hat{\xi}_d$  and the rate of dissipation associated with reaction  $\hat{\xi}_r$ , i.e.,

$$\hat{\xi} = \hat{\xi}_d(\mathbf{F}, \mathbf{q}) + \hat{\xi}_r(C_{\alpha}, r). \quad (6.93)$$

The rate of dissipation associated with the diffusion is assumed to be

$$\hat{\xi}_d = k \left( \frac{1}{J-1} \right)^n \mathbf{q} \cdot \mathbf{q} \quad (6.94)$$

where  $k$  and  $n$  are constant. Usually, reaction between ions, and proton transfers between acids and bases, are very fast [95]. So we assume that the ionic concentration reaches equilibrium instantaneously, so that the rate of dissipation due to reaction is assumed to be zero, i.e.,  $\hat{\xi}_r = 0$ .

From (6.78),  $\tilde{\lambda} = 1/2$ . Substituting (6.82) and (6.93) into (6.75), (6.76) and

(6.77), field equations can be written

$$\operatorname{div}(\hat{\mathbf{T}}) = 0 \quad (6.95)$$

$$\operatorname{grad}\left(\mu + \sum_m \frac{RTC_m}{\rho_{fo}}\right) + \sum_m \frac{RTC_m}{2\rho_{fo}} \operatorname{grad}(z_m^2 k_I \sqrt{I}) = -k \left(\frac{1}{J-1}\right)^n \mathbf{q} \quad (6.96)$$

$$\sum_\alpha s_{k,\alpha} \left(\ln \frac{C_\alpha}{C_\alpha^o} + 1\right) + \sum_i \frac{s_{k,i} z_i^2 k_I}{2} \sqrt{I} = 0 \quad (6.97)$$

where

$$\begin{aligned} \hat{\mathbf{T}} &= \frac{\nu \rho_o RT}{M} (\mathbf{B} - \frac{1}{2} \mathbf{I}) + \frac{RT}{V_o} (\ln(1-\nu) + \nu + \chi \nu^2) \mathbf{I} \\ &\quad - (\rho_{fo} \mu + \sum_m RTC_m + \sum_i \frac{RTC_i}{6} z_i^2 k_I \sqrt{I}) \mathbf{I}. \end{aligned} \quad (6.98)$$

Boundary conditions (6.79) and (6.80) reduce to

$$\hat{\mathbf{T}} \mathbf{n}_1 = \mathbf{t} - \left[ \rho_{fo} \mu_f + RT \sum_m C_{fm} + \sum_m \frac{RT k_I}{6} \sqrt{I_f} z_m^2 C_{fm} \right] \mathbf{n}_1 \quad (6.99)$$

$$\begin{aligned} &\mu + \sum_m \frac{RTC_m}{\rho_{fo}} \left( \ln \frac{C_m}{C_m^o} + 1 + \frac{z_m^2 k_I}{2} \sqrt{I} \right) \\ &= \mu_f + \sum_m \frac{RTC_{fm}}{\rho_{fo}} \left( \ln \frac{C_{fm}}{C_{fm}^o} + 1 + \frac{z_m^2 k_I}{2} \sqrt{I_f} \right) \end{aligned} \quad (6.100)$$

Note that the equation (6.97) gives the equilibrium equation for the  $k^{th}$  reaction.

$$A_k = RT \ln \left( \frac{(C_1^o)^{s_{k,1}} (C_2^o)^{s_{k,2}} \dots}{C_1^{s_{k,1}} C_2^{s_{k,2}} \dots} \right) + \sum_\alpha s_{k,\alpha} - \sum_i \frac{s_{k,i} z_i^2 RT k_I}{2} \sqrt{I} = 0 \quad (6.101)$$

Usually, the ionic strength term in (6.101) is small, i.e.,  $\sum_i \frac{1}{2} s_{k,i} z_i^2 k_I \sqrt{I} \ll 1$ , and the reaction equation (6.101) can be rewritten in reduced form:

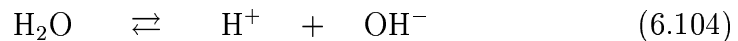
$$RT \ln \left( \frac{K_k^o}{C_1^{s_{k,1}} C_2^{s_{k,2}} \dots} \right) = 0. \quad (6.102)$$

which defines the equilibrium, where  $K_k^o = e^{(s_{k,1} + s_{k,2} + \dots)} \{ (C_1^o)^{s_{k,1}} (C_2^o)^{s_{k,2}} \dots \}$  and is a constant.

## H. Prediction of swelling behavior of anionic hydrogels

### 1. pH dependence of free swelling

We shall investigate the uniform volumetric swelling of carboxylate polymer under no traction in an ionic solution. In order to see the effect of pH value of the solution to the swelling ratio, we first consider a fictitious solution which contains  $\text{H}^+$  and  $\text{OH}^-$  only and the concentration varies arbitrarily. Then, the reaction equations may be given by



The initial position of a particle of the solid is at  $(X, Y, Z)$  and its current position is  $(x, y, z)$ . The deformation is given by

$$x = \nu^{-1/3}X, \quad y = \nu^{-1/3}Y, \quad z = \nu^{-1/3}Z. \quad (6.105)$$

and  $\mathbf{F}$  is  $\nu^{-1/3}\mathbf{I}$ .

When the deformation is homogeneous and the flux  $\mathbf{q}$  is zero, using the deformation field (6.105), we have to solve two equations. A solution can be obtained from the equation (6.95) and the boundary condition (6.99) as

$$\begin{aligned} & \frac{\rho_o RT}{M} \left( \nu^{\frac{1}{3}} - \frac{\nu}{2} \right) + \frac{RT}{V_o} (\ln(1 - \nu) + \nu + \chi\nu^2) = \rho_{fo}(\mu - \mu_f) \\ & + RT(C_{\text{H}^+} + C_{\text{OH}^-} - C_{f\text{H}^+} - C_{f\text{OH}^-}) \\ & + \frac{RTk_I}{6} (\sqrt{I}(C_{\text{ROO}^-} + C_{\text{H}^+} + C_{\text{OH}^-}) - \sqrt{I_f}(C_{f\text{H}^+} + C_{f\text{OH}^-})) \end{aligned} \quad (6.106)$$

where  $I = \frac{1}{2}(C_{\text{H}^+} + C_{\text{OH}^-} + C_{\text{ROO}^-})$  and  $I_f = \frac{1}{2}(C_{f\text{H}^+} + C_{f\text{OH}^-})$ . From the differential

equation (6.96) and the boundary condition (6.100), we obtain

$$\begin{aligned} \rho_{fo}\mu + RT \sum_{i=H^+,OH^-} \left[ C_i \left( \ln \frac{C_i}{C_i^o} + 1 \right) + \frac{C_i}{2} k_I \sqrt{I} \right] \\ = \rho_{fo}\mu_f + RT \sum_{i=H^+,OH^-} \left[ C_{fi} \left( \ln \frac{C_{fi}}{C_i^o} + 1 \right) + \frac{C_{fi}}{2} k_I \sqrt{I_f} \right] \end{aligned} \quad (6.107)$$

Substituting (6.107), (6.106) reduces to

$$\begin{aligned} \frac{\rho_o RT}{M} \left( \nu^{\frac{1}{3}} - \frac{\nu}{2} \right) + \frac{RT}{V_o} (\ln(1 - \nu) + \nu + \chi \nu^2) \\ = \frac{RT k_I}{6} \sqrt{I} C_{\text{RCOO}^-} + \sum_{m=H^+,OH^-} RT \left[ C_{fm} \left( \ln \frac{C_{fm}}{C_m^o} + \frac{k_I}{3} \sqrt{I_f} \right) \right. \\ \left. - C_m \left( \ln \frac{C_m}{C_m^o} + \frac{k_I}{3} \sqrt{I} \right) \right] \end{aligned} \quad (6.108)$$

Boundary conditions for concentration of ionic components are obtained from (6.51)

as

$$\ln \frac{C_{\text{H}^+}}{C_{f\text{H}^+}} = \frac{k_I}{2} \left( \sqrt{\frac{1}{2}(C_{f\text{H}^+} + C_{f\text{OH}^-})} - \sqrt{\frac{1}{2}(C_{\text{H}^+} + C_{\text{OH}^-} + C_{\text{RCOO}^-})} \right) \quad (6.109)$$

$$\ln \frac{C_{\text{OH}^-}}{C_{f\text{OH}^-}} = \frac{k_I}{2} \left( \sqrt{\frac{1}{2}(C_{f\text{H}^+} + C_{f\text{OH}^-})} - \sqrt{\frac{1}{2}(C_{\text{H}^+} + C_{\text{OH}^-} + C_{\text{RCOO}^-})} \right) \quad (6.110)$$

and these equations can be considered as equations for homogeneous swelling problems at equilibrium.

The chemical equilibrium equations (6.101), on combining with (6.36), become

$$\frac{C_{\text{RCOO}^-}}{(c_2 \nu - C_{\text{RCOO}^-}) C_{\text{OH}^-}} = K_1^o \quad (6.111)$$

$$\ln \frac{C_{\text{H}^+} C_{\text{OH}^-}}{K_2^o} = -k_I \sqrt{C_{\text{H}^+} + C_{\text{OH}^-} + C_{\text{RCOO}^-}} \quad (6.112)$$

and (6.111) can be rewritten as

$$C_{\text{RCOO}^-} = \frac{K_1^o c_2 \nu C_{\text{OH}^-}}{1 + K_1^o C_{\text{OH}^-}} \quad (6.113)$$

Solving (6.109), (6.110), (6.112) and (6.113) for  $C_{\text{OH}^+}$  results in

$$\left( \sqrt{C_{f\text{H}^+} + C_{f\text{OH}^-}} - \frac{2\sqrt{2}}{k_I} \ln \frac{C_{\text{OH}^-}}{C_{f\text{OH}^-}} \right)^2 - C_{\text{OH}^-} \left( 1 + \frac{C_{f\text{H}^+}}{C_{f\text{OH}^-}} \right) - \frac{K_1^o c_2 \nu C_{\text{OH}^-}}{1 + K_1^o C_{\text{OH}^-}} = 0. \quad (6.114)$$

When pH value of the solution is given,  $C_{f\text{H}^+}$   $C_{f\text{OH}^-}$  can be calculated as  $10^{-\text{pH}}$  and  $10^{-(14-\text{pH})}$ . The result of solving (6.108) and (6.114) by a numerical method is shown as solid line in Figure 26 which is a plot of the swelling ratio for the different value of pH of the solution.

As we mentioned in the previous section, the effect of ionic strength on the reaction equation is very small. Thus we can use the reduced form of the reaction equation (6.102) and the reaction equations (6.111) and (6.112) can be rewritten in the reduced forms

$$\frac{C_{\text{RCOO}^-}}{(c_2 \nu - C_{\text{RCOO}^-}) C_{\text{OH}^-}} = K_1^o \quad (6.115)$$

$$C_{\text{H}^+} C_{\text{OH}^-} = K_2^o \quad (6.116)$$

and, using (6.36), the equation (6.115) can be written as

$$C_{\text{RCOO}^-} = \frac{K_a c_2 \nu}{C_{\text{H}^+} - K_a} \quad (6.117)$$

where  $K_a = K_1^o K_2^o$ . Also, the right hand sides of (6.109) and (6.110) are very small and can be ignored. Then the relation between  $C_i$  and  $C_{f_i}$  becomes  $C_i = C_{f_i}$ . In stead of solving two non-linear couple equation (6.108) and (6.114), we can substitute (6.117) into (6.108) and solve it with  $C_{\text{H}^+} = C_{f\text{H}^+}$  and  $C_{\text{OH}^+} = C_{f\text{OH}^+}$ . In Figure 26, the dotted line, which is obtained from ignoring the osmotic pressure terms and the electrostatic contribution to chemical equilibrium, is almost identical with the original results. Thus, we find that osmotic pressure effect on the swelling behavior of ionic polymer is negligible.

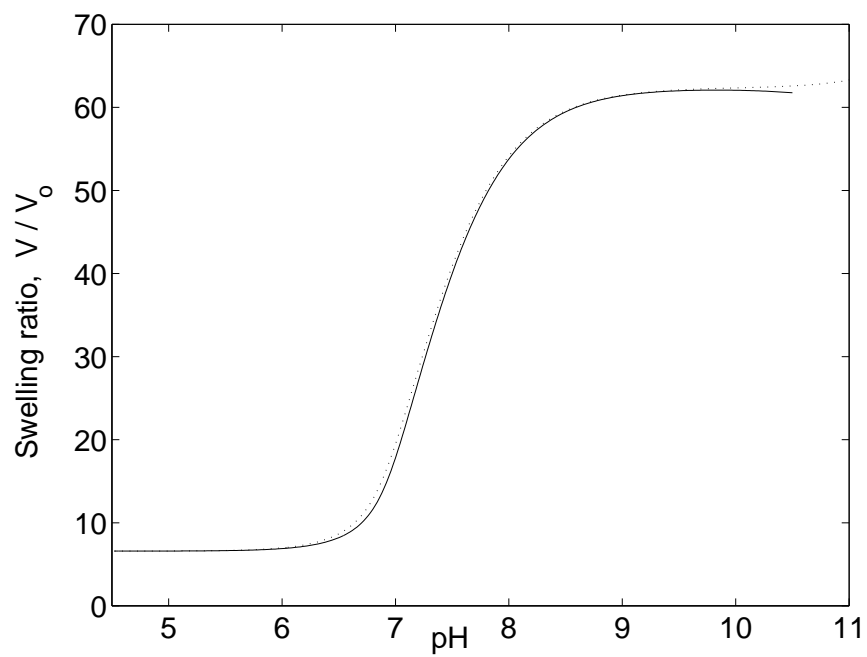


Fig. 26. Swelling ratio of pH-sensitive polymer vs. pH value of the solution (Dotted line shows the result from reduced equations (6.115), (6.116) and (6.117) )

For numerical simulation, the constants corresponding to a typical carboxylated polymer are used

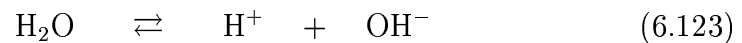
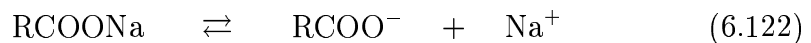
$$\rho_o/M = 6.3 \times 10^{-6} \text{ M/c.c}, \quad c_2 = 36.5 \text{ mM/c.c}, \quad \chi = 0.55 \quad (6.118)$$

$$V_o = 18 \text{ c.c/M}, \quad V_\alpha = \frac{1}{C_\alpha^o} = 22.414 \times 10^3 \text{ c.c/mol}, \quad k_I = 1.17 \text{ M}^{1/2} \quad (6.119)$$

$$pKa = 6.7, \quad R = 8.317 \times 10^7 \text{ dyne-cm/mole} \cdot K^o \quad T = 303 \text{ K}^o \quad (6.120)$$

Figure 27 shows the swelling ratio-pH curves for different values of the initial crosslink density ( $\rho_o/M$ ) and Figure 28 shows the degree of swelling as the pH changes for different  $pKa = -\log(Ka)$  values. The results agree with the qualitative predictions of Brannon-Peppas and Peppas [2]. To obtain the above plot we assumed that mobile ions are  $H^+$  and  $OH^-$  only and the  $H^+$  concentration can be varied arbitrarily. However, realistically the pH value is 7 in a pure water and it can not vary arbitrarily. So, we should take into account the acid anion or the base cation.

Now, we investigate a more practical example. A base NaOH is added to water and all of NaOH is assumed to dissociate in the water. Then the reaction equation can be written as



From (6.102), the equilibrium equations result in

$$\frac{C_{RCOO^-}}{(c_2\nu - C_{RCOO^-})C_{OH^-}} = K_1^o \quad (6.124)$$

$$C_{H^+}C_{OH^-} = K_2^o \quad (6.125)$$

$$\frac{C_{RCOO^-}C_{Na^+}}{C_{RCOONa}} = K_b \quad (6.126)$$



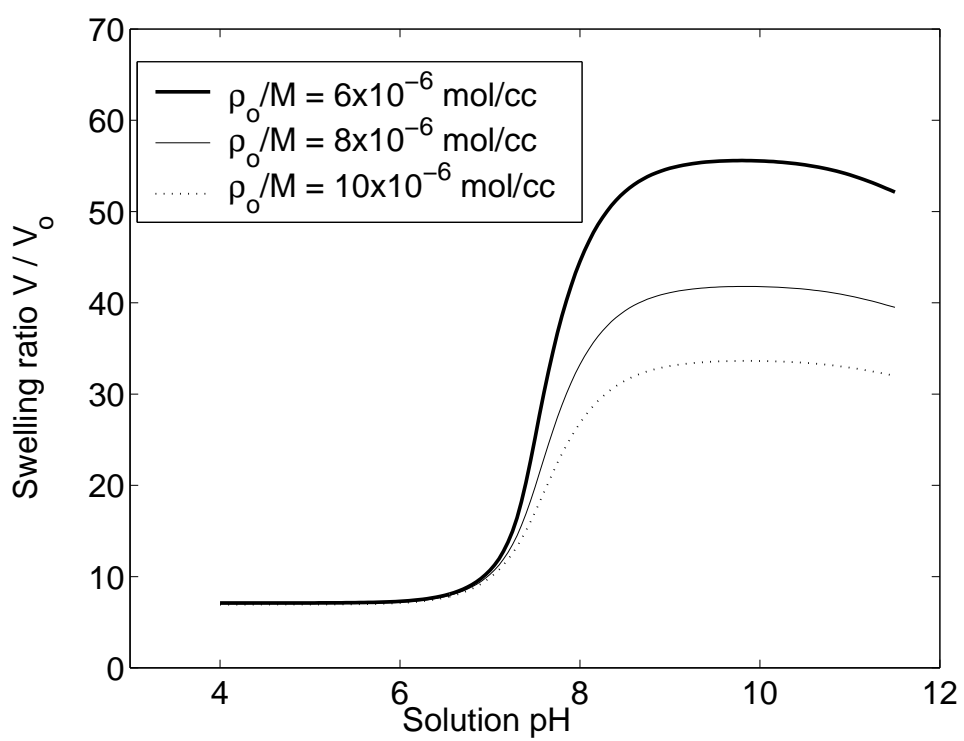


Fig. 27. Theoretical free swelling for different initial crosslink densities ( $\rho_o/M$ )

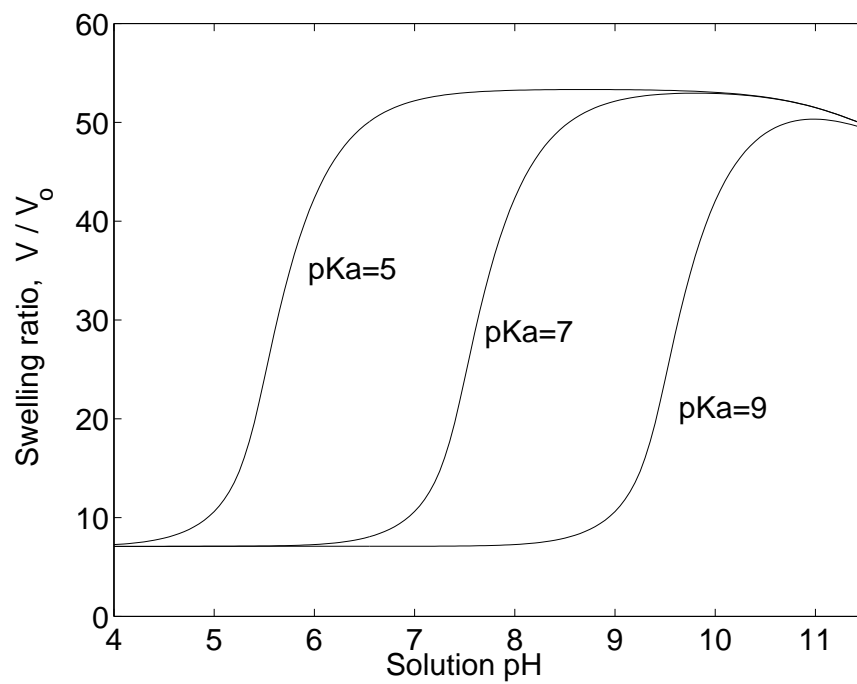


Fig. 28. Theoretical free swelling for different pKa

Together with (6.124–6.125) and  $\nu c_2 = C_{\text{RCOOH}} + C_{\text{RCOONa}} + C_{\text{RCOO}^-}$ , the concentration  $C_{\text{RCOO}^-}$  is obtained as

$$C_{\text{RCOO}^-} = \frac{\nu c_2 K_a}{\frac{K_a}{K_b} C_{\text{Na}^+} + K_a + C_{\text{H}^+}} \quad (6.127)$$

From (6.106), the equation describing the system reduces to

$$\begin{aligned} & \frac{\rho_o RT}{M} \left( \nu^{\frac{1}{3}} - \frac{\nu}{2} \right) + \frac{RT}{V_o} (\ln(1 - \nu) + \nu + \chi \nu^2) \\ &= \frac{RT k_I}{6} \sqrt{I} C_{\text{RCOO}^-} + \sum_m RT \left[ C_{fm} \left( \ln \frac{C_{fm}}{C_{fm}^o} + \frac{k_I}{3} \sqrt{I_f} \right) \right. \\ & \quad \left. - C_m \left( \ln \frac{C_m}{C_m^o} + \frac{k_I}{3} \sqrt{I} \right) \right] \end{aligned} \quad (6.128)$$

where  $m = \{\text{H}^+, \text{OH}^-, \text{Na}^+\}$ ,  $I = C_{\text{RCOO}^-} + C_{\text{H}^+} + C_{\text{OH}^-} + C_{\text{Na}^+}$  and  $I_f = C_{f\text{H}^+} + C_{f\text{OH}^-} + C_{f\text{Na}^+}$ . Concentrations of ionic components at the boundary are given by  $C_{\text{OH}^-} = C_{f\text{OH}^-}$ ,  $C_{\text{H}^+} = C_{f\text{H}^+}$  and  $C_{\text{Na}^+} = C_{f\text{Na}^+}$ .

The dotted-line in Figure 29 is the swelling ratio calculation for a solution which is assumed to have only  $\text{H}^+$  and  $\text{OH}^-$ . It shows that a low constant swelling ratio at low pH values followed by a sharp increase in swelling over a narrow pH range, and at high pH value the swelling ratio is very high and almost constant. The swelling ratio calculation in acetic acid coincides with the dotted-line. In the acid solution, change in concentration of other ions doesn't effect the swelling behavior much. However, in the NaOH base solution, the swelling ratio drops again through increase of pH value. It can be explained as follows, at high pH value, the concentration of  $\text{Na}^+$  increases and starts to associates with  $\text{RCOO}^-$ , and this association decreases the amount of ionized pendant group, and finally decreases swelling ratio. The numerical results show good agreement with the experimental data of Rička and Tanaka [38] as seen from Figure 29.

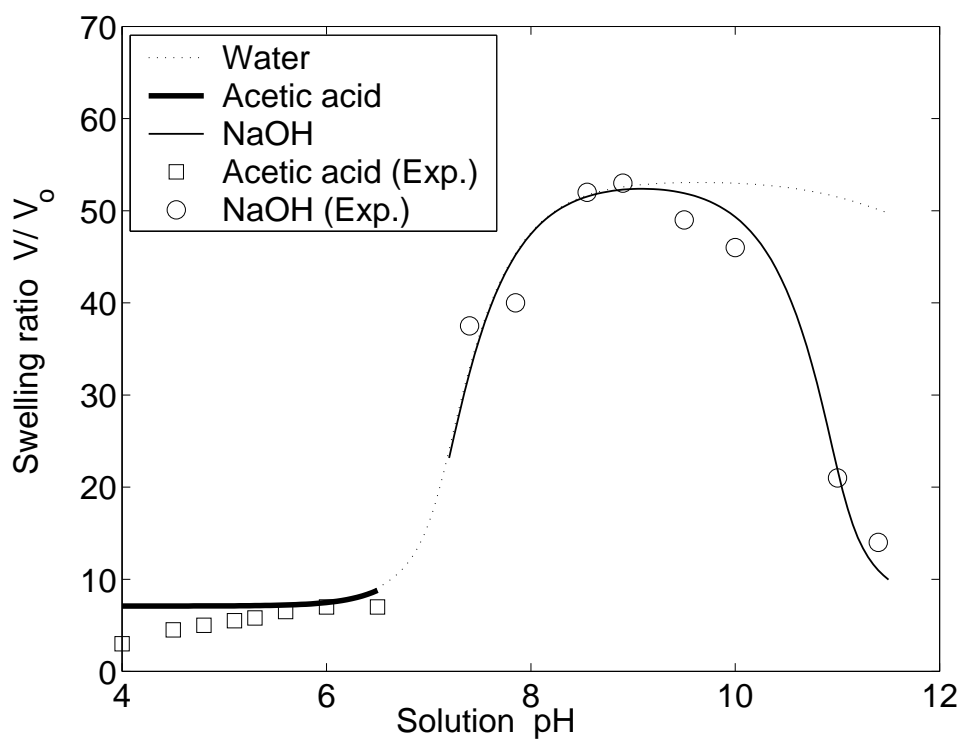


Fig. 29. Theoretical swelling calculation. Experiments by Rička and Tanaka [38] for swelling in solutions of varying pH

## 2. Diffusion through a membrane of an anionic hydrogel

The planes of upstream surface and middle surface are given by  $Z = H_o$  and  $Z = 0$  and the deformation in the hydrogel is given by

$$x = \lambda X, \quad y = \lambda Y, \quad z = f(Z). \quad (6.129)$$

The  $\mathbf{F}$  and  $\mathbf{B}$  are calculated from the deformation as

$$\mathbf{F} = \text{Dia}\{\lambda, \lambda, f'\}, \quad \mathbf{B} = \text{Dia}\{\lambda, \lambda, (f')^2\} \quad (6.130)$$

where  $(\cdot)'$  denotes the derivative with respect to  $Z$  and  $\frac{\partial(\cdot)}{\partial z} = (\cdot)'/f'$ . The volume fraction of the solid  $\nu$  is given by

$$\nu = \frac{1}{f'}. \quad (6.131)$$

The flux  $\mathbf{q}$  is given by

$$\mathbf{q} = \{0, 0, q\}. \quad (6.132)$$

From the conservation of mass equation,  $q$  is a constant for steady state.

The z-components of (6.95) and (6.96) become

$$\begin{aligned} & \frac{1}{f'} \left[ \frac{\rho_o RT}{\eta^2 f' M} \left( (f')^2 - \frac{1}{2} \right) + \frac{RT}{V_o} \left( \ln \left( 1 - \frac{1}{\eta^2 f'} \right) + \frac{1}{\eta^2 f'} + \chi \left( \frac{1}{\eta^2 f'} \right)^2 \right) \right] \mathbf{I} \\ & - \left( RT \sum_m C_m + \frac{RT k_I}{6} \sqrt{I} \sum_i C_i + \rho_{fo} \mu \right) \Big]' = 0 \end{aligned} \quad (6.133)$$

$$\left[ \mu + \sum_m \frac{RT C_m}{\rho_{fo}} \right]' + \sum_m \frac{RT C_m}{\rho_{fo}} \left[ \frac{z_m^2 k_I}{2} \sqrt{I} \right]' = - \frac{k f' q}{(\eta^2 f' - 1)^n} \quad (6.134)$$

The pressure of the upstream fluid and downstream fluid are  $P_u$  and  $P_d$  respectively, and the traction on the upper surface of the hydrogel is zero. Under the assumption that there is no shear on the lateral side, the z-component of the traction of the bottom surface can be found as  $t_z = -(P_u - P_d)$ . The traction boundary conditions

for both  $Z = 0$  and  $Z = H_o$  reduce to

$$\begin{aligned} & \frac{\rho_o RT}{\eta^2 f' M} \left( (f')^2 - \frac{1}{2} \right) + \frac{RT}{V_o} \left( \ln \left( 1 - \frac{1}{\eta^2 f'} \right) + \frac{1}{\eta^2 f'} + \chi \left( \frac{1}{\eta^2 f'} \right)^2 \right) \mathbf{I} \\ & - \left( RT \sum_m C_m + \frac{RT k_I z_m^2}{6} \sqrt{I} \sum_i C_i + \rho_{fo} \mu \right) = -P_u \end{aligned} \quad (6.135)$$

and the boundary conditions for chemical potential reduce to

$$\mu + RT \sum_m \frac{C_m}{\rho_{fo}} \left( \ln \frac{C_m}{C_m^o} + 1 + \frac{z_m^2 k_I}{2} \sqrt{I} \right) = \frac{P_u + \psi_f}{\rho_{fo}} \quad \text{at } Z = H_o, \quad (6.136)$$

$$\mu + RT \sum_m \frac{C_m}{\rho_{fo}} \left( \ln \frac{C_m}{C_m^o} + 1 + \frac{z_m^2 k_I}{2} \sqrt{I} \right) = \frac{P_d + \psi_f}{\rho_{fo}} \quad \text{at } Z = 0. \quad (6.137)$$

In Figure 30 we plot numerical results of flux-pressure difference for the acrylic acid at different pH values. Material parameter  $n = 3$  and  $k = 9 \times 10^7$  dyne-day are used. Figure 30 shows a pH-sensitive switch (see Figure 3(a)). Under non-acidic conditions (high pH), the ionic polymer swells so the diffusion rate of the solution increases. Under acidic conditions (low pH), shrinkage of the polymer occurs, which decreases the membrane permeability, and hence the flux.

## I. Conclusion

We developed a model for the swelling behavior of ionic polymers in the presence of mass flux and chemical reaction using the variational procedure and the limiting procedure based on the assumption of maximum rate of dissipation. By assuming a specific form for the Helmholtz potential due to the charged ion distribution and applying a systematic procedure, we derived three equations for deformation-force equilibrium, mass flux and chemical equilibrium. The results obtained from the equations and boundary conditions shows good agreement with experiments for the equilibrium swelling behavior of an anionic polymer with acrylic pendant groups in acid and basic solutions. Furthermore, it predicts the mass flux-pressure difference

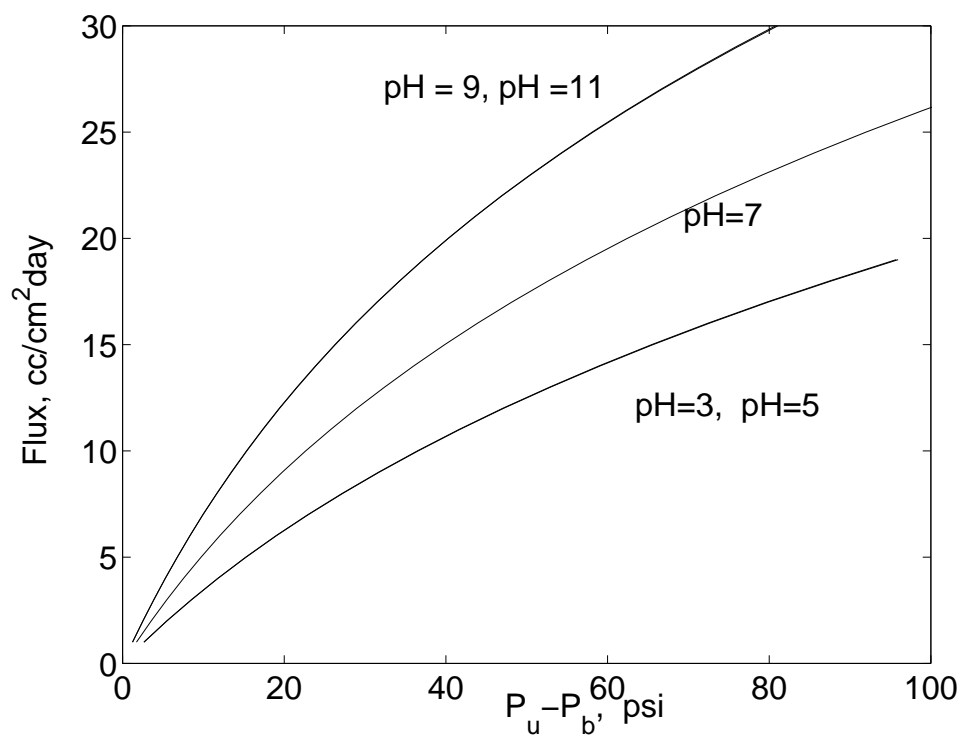


Fig. 30. Flux and pressure difference relationships for a acrylic polymer at different pH values of the solution

relation at different pH values of the solution.



## CHAPTER VII

## CONCLUSION

In the present work, we developed models for the swelling behavior of a rubber-like polymer in the presence of mass diffusion, and the swelling behavior of an ionic polymer in the presence of mass diffusion and chemical reaction. The variational procedure based on the assumption of maximum rate of dissipation and the limiting procedure delivered system equations and boundary conditions out of the specific form of the Helmholtz potential and the rate of dissipation functions, rather than providing the deformation, mass flux and chemical equilibrium equations separately.

Using a specific form of the Helmholtz potential, we found that the result was identical to the Flory-Rehner equation at equilibrium state in the absence of chemical reaction. Then, we showed that the results from a special assumption of the rate of dissipation gave a good agreement with experimental data for diffusion of organic liquids through pure gum rubber sheet. For ionic polymer, the equilibrium swelling behavior of an anionic polymer with acrylic pendant groups in acid and basic solutions was modeled and the numerical results showed good agreement with experimental data. Furthermore, the mass flux-pressure difference relation at different pH values of the solution was predicted.

Here, we did not assume individual diffusion of ions but assumed the diffusion of the solution alone. However, we can assume independent rate of diffusion for each ion, which may give useful models for problems such as selective diffusion control [16] and negative osmotic flows [70]. We can apply the model developed here to problems involving diffusion induced by the different concentration of ions or pH values. We also can apply this model to problems with different geometries and electro-chemical potential fields.

## REFERENCES

- [1] I.Y. Galaev and B. Mattiasson, "'Smart' polymers and what they could do in biotechnology and medicine," *Trends in Biotechnology*, vol. 17, pp. 335–338, 1999.
- [2] L. Brannon-Peppas and N.A. Peppas, "Equilibrium swelling behavior of pH-sensitive hydrogels," *Chemical Engineering Science*, vol. 46, no. 3, pp. 715–722, 1991.
- [3] A.R. Khare and N.A. Peppas, "Swelling/deswelling of anionic copolymer gels," *Biomaterials*, vol. 16, pp. 559–567, 1995.
- [4] M.K. Yoo, Y.K. Sung, Y.M. Lee, and C.S. Cho, "Effect of polyelectrolyte on the lower critical solution temperature of poly(N-isopropyl acrylamide) in the poly(NIPAAm-co-acrylic acid) hydrogel," *Polymer*, vol. 41, pp. 5713–5719, 2000.
- [5] B. Jeong, S.W. Kim, and Y.H. Bae, "Thermosensitive sol-gel reversible hydrogels," *Advanced Drug Delivery Reviews*, vol. 54, pp. 37–51, 2002.
- [6] X. Cao, S. Lai, and L.J. Lee, "Design of a self-regulated drug delivery device," *Biomedical Microdevices*, vol. 3, no. 2, pp. 109–118, 2001.
- [7] M. Shahinpoor and K.J. Kim, "Ionic polymer-metal composites: 1. Fundamentals," *Smart Materials and Structures Journal*, vol. 10, pp. 819–833, 2001.
- [8] M Otake, Y Kagami, M Inaba, and H. Inoue, "Motion design of a starfish-shaped gel robot made of electro-active polymer gel," *Robotics and Autonomous Systems*, vol. 40, pp. 185–191, 2002.

- [9] Y. Osada and M. Hasebe, "Electrically activate mechanochemical devices using polyelectrolyte gels," *Chem. Lett.*, vol. 9, pp. 1285–1288, 1985.
- [10] A.M. Mika, R.F. Childs, and J.M. Dickson, "Salt separation and hydrodynamic permeability of a porous membrane filled with pH-sensitive gel," *Journal of Membrane Science*, vol. 206, pp. 19–30, 2002.
- [11] F. Oosawa, *Polyelectrolytes*, New York: Marcel Dekker, Inc., 1971.
- [12] G. Mamytbekov, K. Bouchal, and M. Ilavsky, "Phase transition in swollen gels 26. Effect of charge concentration on temperature dependence of swelling and mechanical behavior of poly(N-vinylcaprolactam) gels," *European Polymer Journal*, vol. 35, pp. 1925–1933, 1999.
- [13] M. Ilavský, G. Mamytbekov, L. Hanyková, and K. Dušek, "Phase transition in swollen gels 31. Swelling and mechanical behavior of interpenetrating networks composed of poly(1-vinyl-2-pyrrolidone) and polyacrylamide in water/acetone mixtures," *European Polymer Journal*, vol. 38, pp. 875–883, 2002.
- [14] A.M. Mika, R.F. Childs, and J.M. Dickson, "Chemical valves based on poly(4-vinylpyridine)-filled microporous membranes," *Journal of Membrane Science*, vol. 153, pp. 45–56, 1999.
- [15] S.K. Li and A. D'Emanuele, "On-off transport through a thermoresponsive hydrogel composite membrane," *Journal of Controlled Release*, vol. 75, pp. 55–67, 2001.
- [16] J. Hendri, A. Hiroki, Y. Maekawa, M. Yoshida, and R. Katakai, "Permeability control of metal ions using temperature- and pH-sensitive gel membranes," *Radiation Physics and Chemistry*, vol. 60, pp. 617–624, 2001.

- [17] W. Xie and J. Valleton, "Swelling properties of partially hydrolyzed polyacrylamide gels and gelatin gels in aqueous media," *Journal of Membrane Science*, vol. 64, pp. 113–122, 1991.
- [18] W. Hyk, E. Ruiz, and M. Ciszowska, "Transport of uncharged and charged probes in Poly(N-isopropylacrylamide-co-acrylic acid) gels swollen by alcohols: voltametric studies," presented at The 200th Meeting of the Electrochemical Society and the 52th Annual Meeting of the International Society of Electrochemistry-San Francisco, 2001.
- [19] T. Traitel, Y. Cohen, and J. Kost, "Characterization of glucose-sensitive insulin release systems in simulated in vivo conditions," *Biomaterials*, vol. 21, pp. 1679–1687, 2000.
- [20] T. Miyata, T. Uragami, and K. Nakamae, "Biomolecule-sensitive hydrogels," *Advanced Drug Delivery Reviews*, vol. 54, pp. 79–98, 2002.
- [21] K. Sutani, I. Kaetsu, K. Uchida, and Y. Matsubara, "Stimulus responsive drug release from polymer gel. Controlled release of ionic drug from polyampholyte gel," *Radiation Physics and Chemistry*, vol. 64, pp. 331–336, 2002.
- [22] A. Abe, *Neutron Spin Echo Spectroscopy: Viscoelasticity, Rheology*, Berlin: Springer Verlag, 1997.
- [23] P. Gupta, K. Vermani, and S. Garg, "Hydrogels: from controlled release to pH-responsive drug delivery," *Drug Discovery Today*, vol. 7, pp. 569–579, 2002.
- [24] N.F. Sheppard Jr., R.C. Tucker, and S. Salehi-Had, "Design of a conductimetric pH microsensor based on reversibly swelling hydrogels," *Sensors and Actuators B*, vol. 10, pp. 73–77, 1993.

- [25] G. Siegel, M. Malmsten, D. Klüßendorf, A. Walter, F. Schnalke, and A. Kauschmann, “Blood-flow sensing by anionic biopolymers,” *Journal of Autonomic Nervous System*, vol. 57, pp. 207–213, 1996.
- [26] Y. Ueoka, J. Gong, and Y. Osada, “Chemomechanical polymer gel with fish-like motion,” *J. Intelligent Mater. Syst. Struct.*, vol. 8, pp. 465–471, 1997.
- [27] K. Sutani, I. Kaetsu, and K. Uchida, “The synthesis and the electric-responsiveness of hydrogels entrapping natural polyelectrolyte,” *Radiation Physics and Chemistry*, vol. 61, pp. 49–54, 2001.
- [28] I. Kaetsu, K. Uchida, and K. Sutani, “Intelligent feedback release systems and the application to neuron network model research,” *Radiation Physics and Chemistry*, vol. 55, pp. 673–676, 1999.
- [29] H. Nakayama, I. Kaetsu, K. Uchida, S. Sakata, K. Tougou, T. Hara, and Y. Matsubara, “Radiation curing of intelligent coating for controlled release and permeation,” *Radiation Physics and Chemistry*, vol. 63, pp. 521–523, 2002.
- [30] M.H. Holmes, *Mixture Theories for the Mechanics of Biological Tissues*, <http://postulate.math.rpi.edu/~holmes/Mixture/mixture.html>, 1995.
- [31] V.C. Mow, G.A. Ateshian, W.M. Lai, and W.Y. Gu, “Effects of fixed charges on the stress-relaxation behavior of hydrated soft tissues in a confined compression problem,” *International Journal of Solids Structures*, vol. 35, pp. 4945–4962, 1998.
- [32] L.R.G. Treloar, *The Physics of Rubber Elasticity*, London: Oxford at the Clarendon Press, 2 edition, 1958.

- [33] P.J. Flory, *Principles of Polymer Chemistry*, Ithaca, NY: Cornell University Press, 1953.
- [34] P.J. Flory, “Thermodynamics of high polymer solutions,” *Journal of Chemical Physics*, vol. 10, pp. 51–61, 1942.
- [35] M.L. Huggins, “Thermodynamic properties of solutions of long-chain compounds,” *Ann. N.Y. Acad. Sci.*, vol. 43, pp. 1–32, 1942.
- [36] G. Gee, “Some new experimental tests of a statistical thermodynamic theory of rubber-liquid systems,” *Transactions of the Faraday Society*, vol. 42 B, pp. 33–44, 1946.
- [37] P.J. Flory and J.R. Rehner, “Statistical mechanics of cross-linked polymer networks, 2. Swelling,” *The Journal of Chemical Physics*, vol. 11, pp. 521–530, 1943.
- [38] J. Rička and T. Tanaka, “Swelling of ionic gels: Quantitative performance of the Donnan theory,” *Macromolecules*, vol. 17, no. 2916–2921, 1984.
- [39] F.G. Donnan, “The theory of membrane equilibria,” *Chemical Review*, vol. 1, pp. 73–90, 1924.
- [40] A. Katchalsky and I. Michaeli, “Polyelectrolyte gels in salt solutions,” *Journal of Polymer Science*, vol. 15, pp. 69–86, 1955.
- [41] K. Ogawa, Y. Ogawa, and E. Kokufuta, “Effect of charge inhomogeneity of polyelectrolyte gels on their swelling behavior,” *Colloids and Surfaces*, vol. 209, pp. 267–279, 2002.

- [42] P. Gao and M.R. Mackley, "A general model for the diffusion and swelling of polymers and its application to ultra-high molecular mass polyethylene," *Proc. R. Soc. Lond. A*, vol. 444, pp. 267–285, 1994.
- [43] N.A. Peppas and H.J. Moynihan, "Solute diffusion in swollen membranes. IV. Theories for moderately swollen networks," *Journal of Applied Polymer Science*, vol. 30, pp. 2589–2606, 1985.
- [44] K. R. Rajagopal and L. Tao, *Mechanics of Mixtures*, Singapore: World Scientific, 1996.
- [45] J.J. Shi, K.R. Rajagopal, and A.S. Wineman, "Applications of the theory of interacting continua to the diffusion of a fluid through a non-linear elastic media," *Int. J. Engng Sci.*, vol. 19, pp. 871–889, 1981.
- [46] M.V. Gandhi, K.R. Rajagopal, and A.S. Wineman, "Some nonlinear diffusion problems within the context of the theory of interacting continua," *Int. J. Engng Sci.*, vol. 25, no. 11/12, pp. 1441–1457, 1987.
- [47] L. Tao and K.R. Rajagopal, "Unsteady diffusion of fluids through solids undergoing large deformations," *Mathematical Models and Methods in Applied Sciences*, vol. 1, no. 3, pp. 311–346, 1991.
- [48] R.M. Bowen, "The thermochemistry of a reacting mixture of elastic materials with diffusion," *Arch. Rat. Mech. An.*, vol. 34, pp. 97–127, 1969.
- [49] J.W. Nunziato and E.K. Walsh, "On ideal multiphase mixtures with chemical reactions and diffusion," *Arch. Rat. Mech. An.*, vol. 73, pp. 285–311, 1980.
- [50] D.S. Drumheller, "On theories for reacting immiscible mixtures," *Int. J. Engng Sci.*, vol. 38, pp. 347–382, 2000.

- [51] K. R. Rajagopal and A. R. Srinivasa, “Mechanics of the inelastic behavior of materials-Part I: Theoretical underpinnings,” *International Journal of Plasticity*, vol. 118, pp. 945–967, 1998.
- [52] K. R. Rajagopal and A. R. Srinivasa, “Mechanics of the inelastic behavior of materials -Part II: Inelastic response,” *International Journal of Plasticity*, vol. 14, pp. 969–995, 1998.
- [53] K. R. Rajagopal and A. R. Srinivasa, “On the inelastic behavior of solids -Part I: Twinning,” *International Journal of Plasticity*, vol. 6, pp. 653–678, 1995.
- [54] K. R. Rajagopal and A. R. Srinivasa, “On the thermodynamics of shape memory wires,” *ZAMP*, vol. 50, pp. 459–496, 1999.
- [55] K. R. Rajagopal and A. R. Srinivasa, “A thermodynamic framework for rate type fluid models,” *Journal of Non-Newtonian Fluid Mechanics*, vol. 88, pp. 207–227, 2000.
- [56] I. J. Rao and K. R. Rajagopal, “Phenomenological modeling of polymer crystallization using the notion of multiple natural configurations,” *Interfaces and Free Boundaries*, vol. 2, pp. 73–94, 2000.
- [57] G. Gee and L.R.G. Treloar, “The interaction between rubber and liquids. 1. A thermodynamical study of the system rubber-benzene,” *Transactions of the Faraday Society*, vol. 38, pp. 147–163, 1942.
- [58] O. Okay and S. Durmaz, “Charge density dependence of elastic modulus of strong polyelectrolyte hydrogels,” *Polymer*, vol. 43, pp. 1215–1221, 2002.
- [59] J. Hasa, M. Ilavský, and K. Dušek, “Deformational, swelling, and potentiometric behavior of ionized poly(methacrylic acid) gels. I. Theory,” *Journal of Polymer*



- Science*, vol. 13, pp. 253–262, 1975.
- [60] M. Ilavský, J. Pleštil, and K. Dušek, “The photoelastic behavior and small-angle X-ray scattering of ionized gels of copolymers of 2-Hydroxyethyl Methacrylate with Methacrylic acid,” *European Polymer Journal*, vol. 16, pp. 901–907, 1980.
- [61] C. Truesdell and R. Toupin, *The Classical Field Theories*, in *Handbuch der Physik*, vol. 3/1, Berlin: Springer Verlag, 1960.
- [62] R. M. Bowen, “Theory of mixtures,” in *Continuum Physics*, A. C. Eringen, Ed., pp. 1–127. New York: Academic Press, 1975, Volume III.
- [63] R. J. Atkin and R. E. Craine, “Continuum theories of mixtures: Basic theory and historical development,” *Quarterly Journal of Mechanics and Applied Mathematics*, vol. 29, pp. 209–244, 1976.
- [64] N. Mills, “Incompressible mixtures of Newtonian fluids,” *Int. J. Engng Sci.*, vol. 4, pp. 97–112, 1966.
- [65] K.R. Rajagopal, A.S. Wineman, and M. Gandhi, “On the boundary conditions for a certain class of problems in mixture theory,” *Int. J. Engng Sci.*, vol. 24, pp. 1453–1463, 1986.
- [66] F. Dai and K.R. Rajagopal, “Diffusion of fluids through transversely isotropic solids,” *Acta Mech.*, vol. 82, pp. 61–98, 1990.
- [67] R.M. Bowen, “On the stoichiometry of chemically reacting materials,” *Arch. Rat. Mech. An.*, vol. 29, pp. 114–124, 1968.
- [68] Th. De Donder and P. Van Rysselberghe, *Affinity*, Menlo Park, CA: Stanford University Press, 1936.

- [69] W.M. Lai, J.S. Hou, and V.C. Mow, "A triphasic theory for the swelling and deformation behaviors of articular cartilage," *Journal of Biomechanical Engineering*, vol. 113, pp. 245–258, 1991.
- [70] W.Y. Gu, W.M. Lai, and V.C. Mow, "A triphasic analysis of negative osmotic flows through charged hydrated soft tissues," *Journal of Biomechanics*, vol. 30, no. 1, pp. 71–78, 1997.
- [71] A.J.H. Frijns, J.M. Huyghe, and J.D. Janssen, "A validation of the quadriphasic mixture theory for intervertebral disc tissue," *Int. J. Engng Sci.*, vol. 35, no. 15, pp. 1419–1429, 1997.
- [72] H. Ziegler, *Progress in Solid Mechanics*, vol. 4, chapter 2, Amsterdam: North-Holland, 1963.
- [73] K. R. Rajagopal, "Multiple configurations in continuum mechanics," Report Volume 6, Institute for Computational and Applied Mechanics, University of Pittsburgh, Pittsburgh, PA, 1995.
- [74] R.W. Ogden, *Non-linear Elastic Deformations*, New York: Dover, 1997.
- [75] D.R. Paul and O.M. Ebra-Lima, "Pressure-induced diffusion of organic liquids through highly swollen polymer membranes," *Journal of Applied Polymer Science*, vol. 14, pp. 2201–2224, 1970.
- [76] H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, New York: John Wiley & Sons, 1985.
- [77] N.H. Scott, "A theorem in thermoelasticity and its application to linear stability," *Proc. R. Soc. Lond. A*, vol. 424, pp. 143–153, 1989.

- [78] D.J. Gunton and G.A. Saunders, “Stability limits on the Poisson ratio: Application to a martensitic transformation,” *Proc. R. Soc. Lond. A*, vol. 343, pp. 63–83, 1975.
- [79] N.H. Scott, “Thermoelasticity with thermomechanical constraints,” *International Journal of Non-linear Mechanics*, vol. 36, pp. 549–564, 2001.
- [80] N.H. Scott, “Connections between deformation-temperature and deformation-entropy constraints and near-constraints in thermoelasticity,” *Int. J. Engng Sci.*, vol. 34, no. 15, pp. 1689–1704, 1996.
- [81] S. Baek and A.R. Srinivasa, “A variational procedure utilizing the assumption of maximum dissipation rate for gradient-dependent elastic-plastic materials,” *International Journal of Nonlinear Mechanics*, vol. 38, no. 5, pp. 659–662, 2003.
- [82] P. Chadwick, “Thermo-mechanics of rubberlike materials,” *Phil. Trans. R. Soc. Lond. A*, vol. 276, no. 1260, pp. 371–403, 1974.
- [83] L.A. Wood and G.M. Martin, “Compressibility of natural rubber at pressures below 500 kg/cm<sup>2</sup>,” *J. Res. Nat. Bur. Stand.*, vol. 68A, pp. 259–268, 1964.
- [84] H.M. James and E. Guth, “Theory of the elastic properties of rubber,” *The Journal of Chemical Physics*, vol. 11, no. 10, pp. 455–481, 1943.
- [85] A.R. Srinivasa, “Large deformation plasticity and the Poynting effect,” *International Journal of Plasticity*, vol. 17, no. 9, pp. 1189–1214, 2001.
- [86] M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics*, New York: Oxford, 1986.
- [87] J.H. van’t Hoff, “The role of osmotic pressure in the analogy between solutions and gases,” *Zeitschrift für Physikalische Chemie*, vol. 1, pp. 481–508, 1887.

- [88] W.J. Moore, *Physical Chemistry*, Englewood Cliffs, NJ: Prentice-Hall, Inc., fourth edition, 1972.
- [89] I. Prigogine and R. Defay, *Chemical Thermodynamics*, Glasgow: Robert Maclehose and Co., 1954.
- [90] J. Koryta, *Ions, Electrodes, and Membranes*, New York: John Wiley & Sons, 1982.
- [91] A. Katchalsky and S. Lifson, "The electrostatic free energy of polyelectrolyte solutions. I. Randomly kinked macromolecules," *Journal of Polymer Science*, vol. 11, pp. 409, 1953.
- [92] G.S. Manning, "Limiting laws and counterion condensation in polyelectrolyte solutions. I. Colligative properties," *Journal of Chemical Physics*, vol. 51, pp. 924, 1969.
- [93] D. Stigter, "The charged colloidal cylinder with a Gouy double layer," *J. Coll. Int. Sci.*, vol. 53, pp. 296, 1975.
- [94] E.C. Achilleos, K.N. Cristodoulous, and I.G. Kevrekidis, "A transport model for swelling of polyelectrolyte gels in simple and complex geometries," *Computational and Theoretical Polymer Science*, vol. 11, pp. 63–80, 2001.
- [95] T.A. Geissman, *Principles of Organic Chemistry*, San Francisco: W.H. Freeman and Company, fourth edition, 1977.

## APPENDIX A

## VARIATIONAL PROCEDURE USING LAGRANGE MULTIPLIER

In chapter III, a variational procedure to obtain the governing equations of the equilibrium for a swollen solid was developed and the constraint of volume additivity was obtained through a limiting procedure. Here we show another way of imposing constraints using a Lagrange multiplier technique and verify that the final equations and boundary conditions are identical to those in section B.

The time derivative of the volume additivity constraint(3.6) and the equation of conservation of mass for the swollen material are given as

$$\frac{\partial \rho}{\partial t} + \text{grad} \rho \cdot \mathbf{v} + \left( \frac{\rho_o - \rho_{fo}}{J} \right) \text{div} \mathbf{v} = 0 \quad (\text{A.1})$$

$$\frac{\partial \rho}{\partial t} + \text{grad} \rho \cdot \mathbf{v} + \rho \text{div} \mathbf{v} + \text{div} \mathbf{q} = 0 \quad (\text{A.2})$$

Subtracting (A.2) from (A.1) and using (3.6) gives a new equation as

$$\rho_{fo} \text{div} \mathbf{v} + \text{div} \mathbf{q} = 0 \quad (\text{A.3})$$

The incompressibility constraint is expressed as

$$\text{div} \mathbf{v}_f = 0 \quad (\text{A.4})$$

over the region of  $\Omega_f$ .

On the boundary  $\Gamma_m$  the flux  $\mathbf{q}$  is given by

$$\mathbf{q} = \rho_f (\mathbf{v}_f - \mathbf{v}) \quad (\text{A.5})$$

Now we demand that  $\Psi - \int_{\Gamma_f} \mathbf{t} \cdot \mathbf{u}_f dA$  be minimized over the set of all kinematically admissible deformation fields, subject to constraints (A.3), (A.4) and (A.5) over the

set of kinematically admissible displacements of the swollen solid and the fluid with respect to constraints.

Let  $\tilde{\Psi}$  be

$$\begin{aligned} \tilde{\Psi} : &= \Psi - \int_{\Gamma_f} \mathbf{t} \cdot \mathbf{u}_f dA + \int_{\Omega_m} \lambda_1 (\rho_{fo} \operatorname{div} \mathbf{u} + \operatorname{div} \mathbf{q}) dV \\ &+ \int_{\Omega_f} \lambda_2 \rho_{fo} \operatorname{div} \mathbf{u}_f dV + \int_{\Gamma_m} \lambda_3 (\mathbf{q} + \rho_f (\mathbf{u} - \mathbf{u}_f)) dA \end{aligned} \quad (\text{A.6})$$

where  $\lambda_1, \lambda_2$  and  $\lambda_3$  are Lagrange multipliers. Then, utilizing virtual displacements and the divergence theorem  $\delta\tilde{\Psi}$  become

$$\begin{aligned} \delta\tilde{\Psi} &= \int_{\Omega_m} \left( \left[ -\operatorname{div} \left( \frac{\partial\psi}{\partial\mathbf{F}} \mathbf{F}^T \right) - \operatorname{grad}\psi + \operatorname{grad} \left( \rho \frac{\partial\psi}{\partial\rho} \right) - \operatorname{grad}(\rho_{fo}\lambda_1) \right] \cdot \delta\mathbf{u} \right. \\ &\quad \left. + \left( \operatorname{grad} \left( \frac{\partial\psi}{\partial\rho} \right) - \operatorname{grad}\lambda_1 \right) \cdot \delta\mathbf{q} \right) dV \\ &+ \int_{\Omega_f} \left( \left[ -\operatorname{grad}\psi_f + \operatorname{grad} \left( \rho_f \frac{\partial\psi_f}{\partial\rho_f} \right) - \operatorname{grad}(\rho_{fo}\lambda_2) \right] \cdot \delta\mathbf{u}_f \right) dV \quad (\text{A.7}) \\ &+ \int_{\Gamma_m} \left( \left[ \mathbf{F} \left( \frac{\partial\psi}{\partial\mathbf{F}} \right)^T + \left( \psi - \rho \frac{\partial\psi}{\partial\rho} - \psi_f + \rho_{fo}\lambda_1 + \rho_{fo}\lambda_3 \right) \mathbf{I} \right] \delta\mathbf{u} \right. \\ &\quad \left. + \left[ -\frac{\partial\psi}{\partial\rho} + \lambda_1 + \lambda_3 \right] \delta\mathbf{q} + \left[ \rho_f \frac{\partial\psi_f}{\partial\rho_f} - \rho_f \lambda_2 - \rho_f \lambda_3 \right] \delta\mathbf{u}_f \right) \cdot \mathbf{n}_1 dA \\ &+ \int_{\Gamma_f} \left[ \psi_f - \rho_f \frac{\partial\psi_f}{\partial\rho_f} + \rho_f \lambda_2 + P_\infty \right] \delta\mathbf{u}_f \cdot \mathbf{n}_2 dA \end{aligned}$$

where  $\psi = \psi(\mathbf{F}, \rho)$ . Using the fact that  $\delta\tilde{\Psi}$  vanishes for arbitrary  $\delta\mathbf{u}$ ,  $\delta\mathbf{u}_f$  and  $\delta\mathbf{q}$ , we obtain the following differential equations

$$\operatorname{div} \left( -\frac{\partial\psi}{\partial\mathbf{F}} \mathbf{F}^T - \psi + \rho \frac{\partial\psi}{\partial\rho} - \rho_{fo}\lambda_1 \right) = 0 \quad \text{in } \Omega_m \quad (\text{A.8})$$

$$\operatorname{grad} \left( \frac{\partial\psi}{\partial\rho} - \lambda_1 \right) = 0 \quad \text{in } \Omega_m \quad (\text{A.9})$$

$$\operatorname{grad} \left( \psi_f - \rho_f \frac{\partial\psi_f}{\partial\rho_f} + \rho_{fo}\lambda_2 \right) = 0 \quad \text{in } \Omega_f \quad (\text{A.10})$$

and boundary conditions are

$$\left[ \frac{\partial \psi}{\partial \mathbf{F}} \mathbf{F}^T + \left( \psi - \rho \frac{\partial \psi}{\partial \rho} - \psi_f + \rho_{fo} \lambda_1 + \rho_{fo} \lambda_3 \right) \mathbf{I} \right] \mathbf{n}_1 = 0 \quad \text{on } \Gamma_m \quad (\text{A.11})$$

$$\left[ - \frac{\partial \psi}{\partial \rho} + \lambda_1 + \lambda_3 \right] \mathbf{n}_1 = 0 \quad \text{on } \Gamma_m \quad (\text{A.12})$$

$$\left[ \rho_f \frac{\partial \psi_f}{\partial \rho_f} - \rho_f \lambda_2 - \rho_f \lambda_3 \right] \mathbf{n}_1 = 0 \quad \text{on } \Gamma_m \quad (\text{A.13})$$

$$\left[ \psi_f - \rho_f \frac{\partial \psi_f}{\partial \rho_f} + \rho_f \lambda_2 + P_\infty \right] \mathbf{n}_2 = 0 \quad \text{on } \Gamma_f \quad (\text{A.14})$$

Now, we rewrite the constitutive equations for the Helmholtz potential in the form

$$\psi = \psi(\mathbf{F}, \rho(\mathbf{F})) = \tilde{\psi}(\mathbf{F}). \quad (\text{A.15})$$

Then, using the incompressibility constraint of the fluid,  $\rho_f = \rho_{fo}$ , and from the volume additivity constraint, we have

$$\frac{\partial \psi}{\partial \mathbf{F}} = \frac{\partial \tilde{\psi}}{\partial \mathbf{F}} + \frac{(\rho_o - \rho_{fo})}{J} \frac{\partial \psi}{\partial \rho} \mathbf{F}^T \quad (\text{A.16})$$

and defining

$$K = \frac{\partial \psi}{\partial \rho} - \lambda_1, \quad K_f = \frac{\partial \psi_f}{\partial \rho_f} - \lambda_2 \quad (\text{A.17})$$

the differential equations become

$$\text{div} \left( - \frac{\partial \tilde{\psi}}{\partial \mathbf{F}} \mathbf{F}^T + (\rho_{fo} K - \tilde{\psi}) \mathbf{I} \right) = 0 \quad \text{in } \Omega_m \quad (\text{A.18})$$

$$\text{grad}(K) = 0 \quad \text{in } \Omega_m \quad (\text{A.19})$$

$$\text{grad}(\rho_{fo} K_f - \psi_f) = 0 \quad \text{in } \Omega_f \quad (\text{A.20})$$

subject to the boundary conditions

$$\left[ \frac{\partial \tilde{\psi}}{\partial \mathbf{F}} \mathbf{F}^T - (\rho_{fo} K - \tilde{\psi} - \rho_{fo} K_f + \psi_f) \mathbf{I} \right] \mathbf{n}_1 = 0 \quad \text{on } \Gamma_m \quad (\text{A.21})$$

$$[K - K_f] \mathbf{n}_1 = 0 \quad \text{on } \Gamma_m \quad (\text{A.22})$$

$$[\rho_{fo} K_f - \psi_f - P_\infty] \mathbf{n}_2 = 0 \quad \text{on } \Gamma_f. \quad (\text{A.23})$$

These results are the same as (3.39)-(3.44).



## APPENDIX B

## COMPARING FIELD EQUATIONS OF THIS WORK AND MIXTURE THEORY

In this appendix, we show that the differential equations of mixture theory (see Shi et al.[45], Gandhi et al.[46] and Rajagopal & Tao [44]) derived by neglecting inertial effects can be recast into the form (4.17) and (4.18). Whereas in this work we have treated the mixture as a single continuum to derive the equations, in mixture theory the solid constituent  $S_s$  and fluid constituent  $S_f$  are treated separately. Let  $\boldsymbol{\sigma}^s$ ,  $\boldsymbol{\sigma}^f$ , and  $\mathbf{m}$  be the partial stress of  $S_s$ , the partial stress of  $S_f$  and the diffusive body forces. Then the equations for the system in mixture theory are given as

$$\operatorname{div} \boldsymbol{\sigma}^s - \mathbf{m} = 0, \quad (\text{B.1})$$

$$\operatorname{div} \boldsymbol{\sigma}^f + \mathbf{m} = 0, \quad (\text{B.2})$$

in the absence of inertial effect and body forces. As a constitutive relation, the specific Helmholtz free energy (energy per unit mass) is assumed to be

$$A = \hat{A}(\mathbf{F}, \rho_f) \quad (\text{B.3})$$

in mixture theory (whereas in this work the Helmholtz free energy is given by energy per unit volume). The density of the mixture,  $\rho$  is the sum of the density of rubber  $\rho_s$  and the density of fluid  $\rho_f$  in the mixture. The partial stresses  $\boldsymbol{\sigma}^s$ ,  $\boldsymbol{\sigma}^f$  and the

diffusive body force  $\mathbf{m}$  are given by (Gandhi et al. [46, eq. 2.15-32])

$$\boldsymbol{\sigma}^s = \phi \mathbf{I} - \frac{\rho_s}{\rho_{so}} p \mathbf{I} + \rho \frac{\partial A}{\partial \mathbf{F}} \mathbf{F}^T, \quad (\text{B.4})$$

$$\boldsymbol{\sigma}^f = -\phi \mathbf{I} - \frac{\rho_f}{\rho_{fo}} p \mathbf{I} - \rho \rho_f \frac{\partial A}{\partial \rho_f} \mathbf{I}, \quad (\text{B.5})$$

$$\begin{aligned} \mathbf{m} = & \text{grad} \phi - p \text{grad} \left( \frac{\rho_s}{\rho_{so}} \right) + \rho_s \frac{\partial A}{\partial \rho_f} \text{grad} \rho_f \\ & - \rho_f \frac{\partial A}{\partial \mathbf{F}} \text{grad} \mathbf{F} - \alpha \frac{\rho_f \rho_s}{\rho_{fo} \rho_{so}} \mathbf{u}, \end{aligned} \quad (\text{B.6})$$

where  $\rho_{so}$  and  $\rho_{fo}$  are initial densities of the solid and the fluid. The volume additivity requirement gives the equation

$$\rho_f = \rho_{fo} \left( 1 - \frac{1}{J} \right) \quad \text{or} \quad \rho = \rho_{fo} + \frac{\rho_{so} - \rho_{fo}}{J}. \quad (\text{B.7})$$

It follows then that

$$\rho_f = \frac{\rho_{fo}(\rho - \rho_{so})}{\rho_{fo} - \rho_{so}} = \hat{\rho}_f(\mathbf{F}). \quad (\text{B.8})$$

An equation for the total stress is obtained by adding (B.1) and (B.2) and another equation for the fluid is obtained by expanding (B.2) as

$$\text{div} \left( \rho \frac{\partial A}{\partial \mathbf{F}} \mathbf{F}^T - \rho \rho_f \frac{\partial A}{\partial \rho_f} \mathbf{I} - p \mathbf{I} \right) = 0, \quad (\text{B.9})$$

$$\text{grad} \left( p + \rho \rho_{fo} \frac{\partial A}{\partial \rho_f} + \rho_{fo} A \right) = -\alpha \nu \mathbf{u}. \quad (\text{B.10})$$

In chapter IV we have defined the Helmholtz free energy per unit volume  $\psi$  which becomes a function of  $\mathbf{F}$  alone,  $\tilde{\psi}(\mathbf{F})$ , in the limit of volume additivity, and it is given by

$$\tilde{\psi}(\mathbf{F}) = \rho A(\mathbf{F}, \rho_f) \quad (\text{B.11})$$

where  $\rho$  and  $\rho_f$  are functions of  $\mathbf{F}$  from (B.8). Then using the chain-rule, (B.7) and

(B.8), it follows that

$$\begin{aligned}
\frac{\partial \tilde{\psi}}{\partial \mathbf{F}} &= \frac{\partial(\rho A)}{\partial \mathbf{F}} + \frac{\partial(\rho A)}{\partial \rho_f} \frac{\partial \rho_f}{\partial \mathbf{F}} \\
&= \rho \frac{\partial A}{\partial \mathbf{F}} + \left( \rho \frac{\partial A}{\partial \rho_f} + \frac{\rho_{fo} - \rho_{so}}{\rho_{fo}} A \right) \frac{\rho_{fo}}{J} \mathbf{F}^{-T} \\
&= \rho \frac{\partial A}{\partial \mathbf{F}} + \left( \rho(\rho_{fo} - \rho_f) \frac{\partial A}{\partial \rho_f} + (\rho_{fo} - \rho) A \right) \mathbf{F}^{-T}
\end{aligned} \tag{B.12}$$

Substituting (B.12) into (B.9) and (B.10), the equations of system become

$$\operatorname{div} \left( \frac{\partial \tilde{\psi}}{\partial \mathbf{F}} \mathbf{F}^T + \left( \left( 1 - \frac{\rho_{fo}}{\rho} \right) \tilde{\psi} - \rho \rho_{fo} \frac{\partial A}{\partial \rho_f} - p \right) \mathbf{I} \right) = 0 \tag{B.13}$$

$$\operatorname{grad} \left( \frac{\rho_{fo}}{\rho} \tilde{\psi} + \rho \rho_{fo} \frac{\partial A}{\partial \rho_f} + p \right) = -\alpha \nu \mathbf{u} \tag{B.14}$$

Let us define a new variable  $K$  as

$$K = \frac{\tilde{\psi}}{\rho} + \rho \frac{\partial A}{\partial \rho_f} + \frac{p}{\rho_{fo}} \tag{B.15}$$

Then (B.13) and (B.14) become

$$\operatorname{div} \left( \frac{\partial \tilde{\psi}}{\partial \mathbf{F}} \mathbf{F}^T - (\rho_{fo} K - \tilde{\psi}) \mathbf{I} \right) = 0 \tag{B.16}$$

$$\operatorname{grad}(K) = -\frac{\alpha \nu}{\rho_{fo}} \mathbf{u} \tag{B.17}$$

The final form of differential equations (B.16) and (B.17), recast from equations of mixture theory results, are the same as (4.17) and (4.18) obtained in our approach, provided we identify  $\mathbf{q} = \rho_{fo} \mathbf{u}$ . We note that Rajagopal and Tao [44] assume that  $\alpha$  is constant whereas we do not.

## VITA

Seungik Baek was born in Korea in 1971. He graduated with a Bachelor of Science degree in agricultural mechanics and engineering from Seoul National University, Seoul, Korea in January 1996. He received his Doctor of Philosophy degree in mechanical engineering from Texas A&M University in May 2003. The author may be contacted at Jamsil APT. 516-1009, Songpa Gu Seoul, South Korea or through email at [baeksi@hotmail.com](mailto:baeksi@hotmail.com)

The typist for this thesis was Seungik Baek.