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**COMPUTATIONAL INVESTIGATION OF
MAGNETIC HYDROGELS AND ELASTOMERS**

LIU QIMIN

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2019

COMPUTATIONAL INVESTIGATION OF MAGNETIC HYDROGELS AND ELASTOMERS

LIU QIMIN

School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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27/3/19

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Date

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Prof Lam Khin Yong (Main Supervisor)

25 March 2019

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Date

.....
Assoc Prof Li Hua (Co-supervisor)

Authorship Attribution Statement

This thesis contains material from 5 papers published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapter 3 is published as (i) Q. Liu, H. Li, K.Y. Lam, Development of a multiphysics model to characterize the responsive behavior of magnetic-sensitive hydrogels with finite deformation, ACS J. Phys. Chem. B 121(22) (2017) 5633-5646. DOI: 10.1021/acs.jpcc.7b01089. and (ii) Q. Liu, H. Li, K.Y. Lam, Model development and numerical simulation of magnetic-sensitive hydrogels subject to an externally applied magnetic field, Procedia Eng. 214 (2017) 93-97. DOI: 10.1016/j.proeng.2017.09.824.

The contributions of the co-authors are as follows:

- Prof Lam and Assoc Prof Li provided the initial project direction.
- I prepared the manuscript drafts. The manuscript was revised by Prof Lam and Assoc Prof Li.
- I formulated the model with Prof Lam and Assoc Prof Li I also implemented the model into the CMSOL MULTIPHYSICS package and analyzed the numerical results.

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The contributions of the co-authors are as follows:

- Prof Lam and Assoc Prof Li suggested employing the models in relevant applications.
- I wrote the manuscript drafts. The manuscript was revised together with Prof Lam and Assoc Prof Li.

- I formulated the model with Prof Lam and Assoc Prof Li I also implemented the model into the finite element software and analyzed the numerical results.

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- Prof Lam and Assoc Prof Li suggested conducting the project.
- I prepared the manuscript drafts. The manuscript was revised together with Prof Lam and Assoc Prof Li.
- I performed all the numerical simulations including model validation and parameter study.

20/03/2019

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Date

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Abstract

Recently magnetic hydrogels and elastomers attract considerable attention due to their unique characteristics, such as fast response, biocompatibility, and remote actuation. As such, they are used for wide-range applications, such as chemical absorbent, drug delivery, and microfluidics. However, the fundamental mechanism of the magnetic hydrogels and elastomers responsive to the externally imposed magnetic field still remain unclear, due to the lack of efficient models to quantitatively predict their responsive performance with desired accuracy. Therefore, this work aims to develop novel multiphysics models with capability of accurately predicting and characterizing the primary mechanism of the magnetic hydrogels and elastomers in response to the external magnetic field and/or coupled with other stimuli.

The first achievement of the present research work is the development of a multiphysics model for simulation of the responsive behavior of the magnetic-sensitive hydrogel, with the effects of magneto-chemo-mechanical coupled fields, which is termed the multi-effect-coupling magnetic-stimulus (MECm) model. In this model, the magnetic susceptibility for magnetization of the general magnetic hydrogel is defined as a function of finite deformation, instead of a constant for an ideal magnetic hydrogel. The constitutive equations, formulated by the second law of thermodynamics, accounts for the effects of the chemical potential, the externally applied magnetic field, and the finite deformation. In particular, a novel free energy density is proposed with consideration of magnetic effect associated with finite deformation, instead of volume fraction. After examination with published experimental data, it is confirmed that the MECm model can well capture the responsive behavior of the magnetic hydrogel, including the deformation

and its instability and hysteresis under a uniform or nonuniform magnetic field. The parameter studies for optimized design of the magnetic hydrogel are then carried out for influences of various material properties and magnetic parameters, including shear modulus, magnetic intensity, and volume fraction of the magnetic particles, on the behavior of the magnetic hydrogel in the equilibrium state, for a deeper insight into the fundamental mechanism of the magnetic hydrogels.

The second achievement is the extension of the MECm model for characterization of the transient fluid-structure interaction of the deformable magnetic hydrogel with surrounding fluid flow, through the fully coupled arbitrary Lagrangian-Eulerian (ALE) algorithm. The extended model is validated by comparing with both the published finite difference result and experimental data, where good agreements between them are achieved. It is verified that the present model enables to predict the transient performance of the magnetic hydrogel placed in moving fluid. Furthermore, two magnetic hydrogel-based devices are designed and optimized by the extended model. The first is the magnetic hydrogel-based microfluidic system for replicating various physiological and pathological conditions in the human body, by which the desired flow patterns can be generated in real time due to the fast-response deformation of the magnetic hydrogel. The second device is the magnetic hydrogel-based drug targeting system for delivering the movable and deformable drug-loaded hydrogel to the specific site by variation of the inlet fluid flow velocity, the hydrogel size and position, the maximum magnetic field strength, and magnet position.

The third achievement is the development of a multi-effect-coupling magnetic-pH-stimuli (MECmpH) model for optimization of cell physiological microenvironment within the magnetic-pH-sensitive hydrogel-based scaffold. In particular, the positions of seeding cells and the concentration of potassium (K^+) within the scaffold are optimized by the MECmpH model, based on (i) the threshold of mechanical force for mechanotransduction effect at cellular-size level, and (ii) the common biological requirement for the cell growth. In the MECmpH model, the four responsive mechanisms of the magnetic hydrogel are characterized, including hydrogel magnetization, ionic polarization, diffusions of the solvent and ions, and nonlinear finite deformation, when subjected to various biophysical and biochemical stimuli, such as the magnetic field due to current intensity and the solution pH. After validation of the MECmpH model with experimental data in open literature, it is found that the higher pH level and current intensity, and the shorter hydrogel-magnet distance contribute to the larger deformation of the magnetic scaffold and thus the stronger mechanical force on cells. Moreover, the cell seeding positions within magnetic scaffold are optimized for better cell culture through the controllable current intensity. Furthermore, the physiological concentration of K^+ within the scaffold is also optimized through initial fixed charge density within the scaffold.

The last achievement is the development of a magneto-mechanical model for magnetic elastomer microactuator, where the transition is investigated between the uniform and nonuniform magnetic fields and the field-induced nonlinear deformation, due to reversible variation of the geometric size of the magnetic elastomer from infinite to finite one. In this study, both the elastomer and its surrounding medium are covered in

the computational domain, where the Maxwell stress over the elastomer-surrounding interface is considered as an additional mechanical boundary, and the nonlinear magnetization included in a proposed free energy density. After validation of the present model with both the published theoretical and experimental works, it is concluded that increasing the geometric size of the magnetic elastomer leads to a more uniform magnetic field, and thus the elastomer undergoes the transition from the nonuniform to uniform magnetic fields, if its size increases to a critical point.

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List of Symbols

A	magnetic vector potential
b, B	magnetic induction vector in current, reference configuration
C	right Cauchy-Green tensor
C	chemical energy
C_f^0	nominal concentration of fixed charges within hydrogel at dry state
C_k	nominal ion concentration
c_s, C_s	true, nominal concentration of solvent
D	electric displacement vector
D_s	diffusion coefficient
E	electric intensity vector
e, E	the total energy per unit current, reference volume
F	deformation gradient
F, Φ, Ω, Ψ	(augmented) free energy density
$\mathbf{f}_b$	body force per mass
f_H	external magnetic field frequency
$\mathbf{f}_m$	magnetic body force per mass
F_r	Faraday's constant
$g(\mathbf{r})$	spatial pair distribution function
h, H	magnetic intensity vector in current, reference configuration
$\mathbf{H}_d$	inner demagnetization field
$\mathbf{H}_d'$	demagnetization field of the particle
$\mathbf{H}_i$	internal magnetic field
$\mathbf{H}_0$	external magnetic intensity
$\mathbf{h}_p$	magnetic field inside a magnetic particle
$\langle \mathbf{h}_p \rangle$	volume average magnetic field over the position of every particle
I	second rank identity tensor
J	determinant
$\mathbf{J}_k$	nominal ionic flux
$\mathbf{j}_s, \mathbf{J}_s$	true, nominal diffusion flux of solvent

K	kinetic energy
k_B	Boltzmann constant
K_d	dissociation constant
$\mathbf{m}, \mathbf{M}$	magnetization vector in current, reference configuration
M	magnetization energy
$\mathbf{M}_p$	particle magnetization
m_p	magnetic moment of the particle
m_s, m_{sat}	saturation magnetization of magnetic elastomer, particle
$\mathbf{n}, \mathbf{N}$	unit outward normal to the current, reference surface boundary
N	effective number of polymer chains per unit reference volume
N_d	demagnetizing factor of magnetic hydrogel
N_x, N_y, N_z	demagnetizing factor along x -, y -, z -axis
p	fluid pressure
P_x, P_y, P_z	stress in x -, y -, z - axis
$\mathbf{q}, \mathbf{Q}$	true, nominal heat flux vector
Q	thermal energy
R_k	rate generation of the k th mobile species
r_q, R_q	rate of true, nominal heat generation in a control volume
r_s, R_s	rate of true, nominal mass supply in a control volume
T	absolute temperature
$\mathbf{T}_a, \mathbf{T}_m$	mechanical, magnetic traction
U	internal energy
$\mathbf{u}$	hydrogel displacement
$\mathbf{V}_h$	deformation velocity
$\mathbf{v}_s$	convection fluid flow velocity
w	fluid flow rate
W	mechanical work
$\mathbf{x}, \mathbf{X}$	Eulerian, Lagrangian coordinate
z_f, C_f	valence, concentration of the fixed charges
z_k, C_k	valence, concentrations of the mobile ions
μ_0	magnetic permeability in a vacuum

μ_m	magnetic permeability of magnetic hydrogel
μ_{mr}	relative magnetic permeability of magnetic hydrogel
$\mathbf{\mu}_m$	magnetic permeability tensor
μ_{m0}, χ_{m0}	initial magnetic permeability, susceptibility
μ_s	chemical potential of solvent
ξ_p	volume fraction of magnetic particles
ϕ_s^0	volume fraction of polymeric network at reference state
ρ_h, ρ_0	true, nominal mass density of the hydrogel
$\boldsymbol{\sigma}, \mathbf{P}$	Cauchy, first Piola-Kirchhoff stress tensor
$\boldsymbol{\sigma}_m, \mathbf{P}_m$	Maxwell stress tensor in Eulerian, Lagrangian form
$\mathcal{E}$	total energy in hydrogel system
$\epsilon_0, \epsilon_{er}$	dielectric permittivity in vacuum, medium
η	entropy per unit volume
v_s	volume per solvent species
Π	Lagrange multiplier or osmotic pressure
χ	magnetic susceptibility of magnetic hydrogel
χ_0	initial magnetic susceptibility of magnetic hydrogel
χ_H	Flory-Huggins parameter
χ_p	magnetic susceptibility of the magnetic particle
$\lambda_x, \lambda_y, \lambda_z$	stretch in x-, y-, z- axis
ζ	Langevin parameter
ρ_s	density of fluid
$\boldsymbol{\sigma}_s$	fluid stress tensor
φ	dynamic viscosity
ϕ, ψ	electric, magnetic scalar potential

Chapter 1. Introduction

1.1. Background

Life is intrinsically polymeric: the most significant elements of a living cell (carbohydrates, protein, and nucleic acids) are all polymers [1]. As a typical soft material, the elastomer consists of a three-dimensional (3D) network of long and flexible polymer molecules which interact with each other at certain point along their length [2]. The interaction point is called cross-link. The basic elements of the polymeric network are called chains, which are the parts of molecules reaching from one crosslinkage to the next. When the elastomer is stretched, the elastic force arises due to the decrease of configurational entropy of the polymer chains.

Elastomeric gel or hydrogel is another kind of soft materials, which is not dry and stiff as the elastomer. It contains large quantities of solvent due to hydrophilic groups attached to the polymeric chains, such that the interstitial fluid and polymer chains constitute the main components of the hydrogel [3]. Inside the hydrogel, the solid chains are crosslinked each other through various bonds, including covalent bond, van der Waals force, hydrogen bond, electrostatic interaction, and physical entanglement [4]. The elastic networks provide the structural integrity of the hydrogels, which ensures the hydrogels showing thermodynamic compatibility with fluid, and allows them to swell in aqueous media [5]. The interstitial fluid fills up the pores within the networks and determines the overall permeation of substances into and out of the hydrogel [6]. As a result of the peculiar network structure, the hydrogel owns both the solid- and liquid-like properties, and is able to absorb abundant water or biological fluid [7].

Based on the preparation methods, ionic charges, and nature of crosslinking, hydrogels are divided into many categories. For example, depending on different monomers employed to form the polymeric structure, hydrogels are classified into homopolymers, copolymers, and interpenetrating polymers [8]. On the basis of the characteristics of side groups attached to polymer chains, they are categorized into neutral, ionic, and amphoteric hydrogels. Hydrogels are also labeled as chemical or physical hydrogels according to the crosslinking nature. Usually chemical hydrogels are stable mechanically and thermally and cannot be dissolved in solution, unless the covalent crosslink junctions are cleaved [9]. Physical hydrogels are often crosslinked by weak physical bonds including hydrogen bonding and van der Waals interactions, such that they may be degraded and eventually disintegrated and dissolved [6].

Some hydrogels can undergo relatively large and reversible swelling when subjected to subtle variations of the external stimuli, including pH, light, enzyme, temperature, ultrasound, and electric field [10-14]. These hydrogels are often called stimulus-responsive hydrogels [15], intelligent hydrogels [16], or smart hydrogels [17]. Due to the unique autonomous characteristics of smart hydrogels, including significant solvent content, high ionic conductivity, and excellent biocompatibility, smart hydrogel attracts considerable attentions from researchers and is increasingly playing important roles in wide-range applications, such as biosensors [15], microfluidic devices [18], actuators [19, 20], as well as drug delivery and release [21].

Despite the attractive merits, several limitations still exist in current smart hydrogel systems owing to the slow response process, limited mechanical strength, and poor

actuation and controllability [22]. For example, the response time may be as long as several hours for hydrogel swelling [20]. The behavior of the conventional hydrogel is hard to control, owing to the direct contact between the hydrogel and external stimuli [22]. The disadvantages often hinder researchers from developing optimum hydrogel for potential applications. Thereby, hydrogels with excellent actuation, controllability, and response features are required [22].

Over the past decades, significant advances were achieved in development of magnetic hydrogel, which is composed of soft polymeric matrix filled with water and magnetic particles. The magnetic hydrogel was firstly introduced by Zrínyi in 1995 [23] and was also termed ferrogel [24] and ferrohydrogel [25], where magnetic particles with micro- or nano-sizes are commonly used since they are easily magnetized and aggregated in a specific site through imposing an external magnetic field, and redispersed rapidly when removing the field [26]. Magnetic hydrogel deforms silently, responses fast, and can be actuated remotely, such that they are very promising in several applications, such as chemical adsorbent [27], microfluidic valve [28], and drug delivery [29].

Currently magnetic hydrogels were prepared into many categories. For example, when magnetic particles are incorporated into a neutral hydrogel without charge groups, the hydrogel is sensitive to external magnetic field and it becomes a magnetic-sensitive hydrogel [30]. When particles are embedded into a pH- sensitive or temperature-sensitive hydrogel, the hydrogels exhibit dual-responsive characteristics and results in magnetic-pH-sensitive hydrogels or magnetic-temperature-sensitive hydrogels [31, 32]. Apart from the three main types of magnetic hydrogels mentioned above, the multi-responsive

magnetic hydrogels were also developed to show sensitivity to multiple external stimuli, including magnetic-pH-temperature-sensitive hydrogels and magnetic-ion strength-sensitive hydrogels [33-36].

1.2. Motivation and objectives

As the novel hybrid magnetic materials, the applications of magnetic elastomers and hydrogels are being expanded rapidly. For example, they were widely employed as adsorbents in the field of environmental improvement [27, 37-40], and commonly used in drug delivery and enzyme immobilization systems [22]. They were good candidates for microactuator in the fields of microfluidics and microelectromechanical systems (MEMS) devices [28]. Moreover, they were also demonstrated to be prominent heat agents in tumor therapies where precise temperature controls are required [41, 42].

The applications of magnetic hydrogels and elastomers rely much on the comprehensive understanding of their physical properties and responsive mechanisms, such as the hydrogel or elastomer magnetization, solvent diffusion in hydrogel, and nonlinear deformation of hydrogel or elastomer. However, a fundamental understanding of these soft magnetic materials is still preliminary. In particular, most relevant investigations were experiment-based and thus time-consuming, such that they may not fully capture all the effects on the behavior of these materials.

As an alternative option, theoretical modeling is expected to well characterize the performance of magnetic hydrogels and elastomers. In accordance with the literature review in Chapter 2, it is found that several models at different length scales were developed for magnetic elastomers placed in air environment and assumed an

incompressible elastomer with constant volume [43-45]. Usually the homogeneous magnetic field and field-induced deformation are considered to simplify the theoretical analysis, where the elastomer with infinite geometric size is employed and the computational domain merely covered the elastomer, i.e. the influences of the surrounding and interface were neglected. However, usually the elastomer with finite size was used in the experiment, where the surrounding and the interface may play crucial roles in its responsive behavior. Consequently, a significant discrepancy was found between the model prediction and experimental result [46, 47]. The inconsistency remains unclear, probably due to lack of a robust magneto-mechanical model for quantifying the distributive magnetic field and field-induced nonlinear deformation, which are associated with the magnetic elastomer geometry.

Different from the theoretical works on magnetic elastomer in air surrounding with constant volume during its deformation, the modeling of magnetic hydrogel focuses on the deformable hydrogel placed in a solvent/solution environment, where the hydrogel imbibes large quantities of solvent/solution, which is characterized by a chemical field, and significant volume change described by a mechanical equilibrium field. A literature search reveals that so far only one theoretical work for a magnetic hydrogel submerged in a solvent, under a uniform magnetic field in the equilibrium state, was published to predict the swelling via its volume fraction ratio only [30], meaning that the present hydrogel swelling deformation is a scalar, instead of a vector. Therefore, it is unable to characterize the deformation of the magnetic hydrogel appropriately. Recently relevant experimental works were conducted for the deformable magnetic hydrogel. However, the results seem to be contradictory to each other qualitatively. For example,

some of them showed that the hydrogel in a uniform magnetic field elongated along the field direction and contracted in the transverse direction [48, 49], while another experiment demonstrated contraction along the field direction [50]. The contradiction remains unclear, probably due to the lack of an efficient model to characterize the mechanism of the magnetic hydrogel.

Therefore, the objective of the present research work focuses on development of multiphysics models to characterize the fundamental mechanisms of the magnetic hydrogels and elastomers in response to the magnetic and/or other coupled physical fields. The specific objectives and the corresponding scopes are summarized below.

- Development of a multiphysics model for simulation of the performance of the magnetic-sensitive hydrogel, with the effects of magneto-chemo-mechanical coupled fields, which is called the multi-effect-coupling magnetic-stimulus (MECm) model. The responsive mechanisms are considered in this model, including the hydrogel magnetization, solvent diffusion, and hydrogel large deformation, where the magnetic susceptibility for magnetization of a general magnetic hydrogel is defined as a function of finite deformation, instead of a constant for an ideal magnetic hydrogel. The MECm model is examined by the published experimental data in open literature. For optimized design of the magnetic hydrogel, the influences of the material properties and magnetic parameters are conducted, including the shear modulus, magnetic intensity, and particle volume fraction, on the equilibrium behavior of magnetic hydrogel.
- Extension of the MECm model for characterization of the transient fluid-structure interaction of the deformable magnetic-sensitive hydrogel with surrounding fluid

flow, through the fully coupled arbitrary Lagrangian-Eulerian (ALE) algorithm. The extended model includes the hydrodynamic effect by the incompressible Navier-Stokes equations. It is examined by comparing with both finite difference result and published experimental data, where satisfactory agreements between them are reached. Furthermore, two magnetic hydrogel-based devices are designed and optimized via the extended multiphysics model. The first is the magnetic hydrogel-based microfluidic system for replicating various physiological and pathological conditions in the human body, by which the desired flow patterns can be generated in real time due to the fast-response deformation of the magnetic hydrogel. The second one is the magnetic hydrogel-based drug targeting system for delivering the deformable drug-loaded hydrogel in suspension fluid to the specific site by variation of the inlet fluid flow velocity, the maximum magnetic field strength, magnet position, as well as the hydrogel size and position.

- Development of a multi-effect-coupling magnetic-pH-stimuli (MECmpH) model for optimization of cell physiological microenvironment within the magnetic-pH-sensitive hydrogel-based scaffold. In the MECmpH model, the four responsive mechanisms of the magnetic hydrogel are characterized, including hydrogel magnetization, ionic polarization, diffusions of the solvent and ions, and nonlinear finite deformation, when subjected to various biophysical and biochemical stimuli, such as the magnetic field due to current intensity and the solution pH. In particular, the positions of seeding cells and the concentration of potassium (K^+) within the scaffold are optimized by the MECmpH model, based on (i) the threshold of mechanical force for mechanotransduction effect at cellular-size level, and (ii) the

common biological requirement for the cell growth. After verification of the MECmpH model with experimental result in the open literature, the mechanical force acting on cells are predicted quantitatively when subject to varying pH level, current intensity, and the hydrogel-magnet distance. Furthermore, the physiological concentration of K^+ within the scaffold is also predicted by variation of the initial fixed charge density.

- Development of a magneto-mechanical model for magnetic elastomer microactuator, where the transition is investigated between the uniform and nonuniform magnetic fields and the field-induced nonlinear deformation, due to reversible variation of the geometric size of the magnetic elastomer from infinite to finite one. In this model, both the elastomer and its surrounding medium are covered in the computational domain, where the Maxwell stress over the elastomer-surrounding interface is considered as an additional mechanical boundary, and the nonlinear magnetization included in a proposed free energy density. After validation of the present simulation with both the theoretical and experimental works in open literature, the magnetic field distribution and the field-induced nonlinear deformation are characterized due to variation of the geometric size of the elastomer. Furthermore, the critical elastomer size is determined for the transition from the nonuniform to uniform magnetic fields.

1.3. Thesis outline

This thesis is composed of seven chapters, detailed as follows.

Chapter 1 introduces the backgrounds of the magnetic hydrogels and elastomers, states the motivations to develop multiphysics models, and then presents the research objectives, followed by the thesis outline.

Chapter 2 provides a literature review of the experimental and theoretical works on soft magnetic materials including magnetic elastomers and magnetic hydrogels.

Chapter 3 develops a multi-effect-coupling magnetic-stimulus (MECm) model for the magnetic-sensitive hydrogel subject to the magneto-chemo-mechanical coupled fields. The MECm model is firstly reduced to study the response the magnetic-sensitive hydrogel in the equilibrium state, and then extended to consider the transient fluid-structure interaction of the deformable magnetic-sensitive hydrogel with surrounding fluid flow, followed by validation with several experimental and theoretical works from the literature. The MECm model will be employed in Chapter 4 to analyze and optimize the property of magnetic-sensitive hydrogel and the relevant hydrogel-based devices.

Chapter 4 elaborates the optimized designs of the magnetic-sensitive hydrogel by the MECm model in the equilibrium state, and the magnetic-sensitive hydrogel-based devices by the transient extended MECm model with moving fluid.

Chapter 5 develops a multi-effect-coupling magnetic-pH-stimuli (MECmpH) model for optimization of cell physiological microenvironment within the dual magnetic-pH-sensitive hydrogel-based scaffold, and then validates the theoretical model with experimental works in open literature.

Chapter 6 develops a magneto-mechanical model for magnetic elastomer microactuator, where the transition is investigated between the uniform and nonuniform magnetic fields and the field-induced nonlinear deformation, due to reversible variation of the geometric size of the magnetic elastomer from infinite to finite one.

Chapter 7 summarizes the main contributions of the present research work and recommends possible future work.

Chapter 2. Literature Review

The invention of magnetic polymer may be enlightened by the idea of magnetorheological fluid (MRF), where the fluid is employed as the carrier of the magnetic particles [51]. Without an external magnetic field, magnetic particles at micro- or nano-level are randomly dispersed in the fluid. When an external magnetic field is imposed, a chain-like structure is instantly formed, due to the particle magnetization and the particle-particle interaction. The regulated microstructure increases the stiffness and yield strength of the MRF and thus show promise for engineering applications including shock absorbers, shakes, and control valves [52]. However, the MRF may suffer from sedimentation due to the density mismatch between liquid carrier and particles [53], environmental contamination due to the liquid leakage, and performance degradation due to the particle residue [54]. Moreover, the extra container is needed to maintain the MRF in its position [55]. To overcome the disadvantages, the magnetic polymer is developed, in which the nonmagnetic solid networks are employed as the matrices to hold the magnetic particles.

Over the past decades, different types of magnetic polymers were developed including pure molecular magnets and magnetic polymer composites [56]. Molecular magnet is a well-known magnetic material at molecular scale which shows a combination of desirable properties unavailable in conventional metal/intermetallic and metal-oxide magnets, including superparamagnetism, low weight, high magnetization, as well as low-temperature fabrication [57]. However, the current molecular magnet developed only remains laboratory curiosities without real-world application due to the very low

responsive temperature [56]. As a typical magnetic polymer composite, the magnetic plastic consists of rigid polymers embedded with magnetic particles, which was employed as permanent plastic magnet, magnetic core, as well as connecting and fixing element [58]. Nevertheless, the application of the magnetic plastic is still restricted in many areas [58], where high flexibility and large shape change are required. To overcome it, the magnetic composite is developed by combination of soft polymer and magnetic particles, including the magnetic hydrogel and elastomer. As mentioned previously, the magnetic hydrogel belongs to a subclass of the magnetic elastomer [3], since the hydrogel may be achieved by submerging the hydrophilic elastomer in aqueous media. In the present work, the magnetic hydrogel and elastomer are regarded as two different magnetic composites, since the former often works in aqueous solution while the latter in air environment. Furthermore, the volume of the magnetic elastomer remains unchanged during its deformation [58], while both volume and shape are changed significantly in magnetic hydrogel [49, 59]. As mentioned previously, the magnetic hydrogels are further classified into many categories based on the carriers of the particles, such as the neutral hydrogel, the pH-sensitive hydrogel, the temperature-sensitive hydrogel, as well as other environmental-sensitive hydrogels. Therefore, the family of magnetic polymer in the present study is demonstrated in Figure 2.1.

Figure 2.1. The family of the magnetic polymer.

2.1. Experimental investigation on magnetic elastomer

Magnetic elastomer is a polymer-based hybrid material embedded with magnetic particles, which usually works in an air environment [43]. Various polymers were adopted to synthesize the magnetic elastomers, such as Polyvinyl alcohol (PVA) [60], Polydimethylsiloxane (PDMS) [24, 56], and natural rubber [54, 61]. To reduce the disturbance on particle magnetization, the magnetic permeability of the polymer is required to be as low as possible [55]. Usually the particles embedded are soft magnetic materials, such as iron powders [62], carbonyl iron [58, 63], nickel [64], and magnetite [65], due to their high permeability and saturation magnetization, and low remnant magnetization. The bonding between particles and polymer segments includes hydrogen bond [66], coordination bond [67], electrostatic attraction [68], and covalent attachment [25, 69-72]. The particles are even directly adopted as the cross-linkers [25, 73-76] to avoid the particles migration out of the polymer matrix.

In general, magnetic elastomers are mainly divided into two categories by distribution of particles. An isotropic magnetic elastomer, cured without a magnetic field,

has particles randomly distributed in the polymer matrix [77], as shown in Figure 2.2 (a). An anisotropic magnetic elastomer however, cured with a uniform magnetic field, has particles parallel to field direction [78], as illustrated in Figure 2.2 (b). Usually the anisotropic arrangements are preserved even the external magnetic field is removed, because the chain-like structures are locked in the matrix upon completion of the polymerization [79]. It was reported that the deformation in isotropic magnetic elastomer may be one order of magnitude larger than that in anisotropic one [80]. Furthermore, the strain is much dependent on the magnetic field applied. For example, it may be proportional to the square of magnetic intensity when a very low magnetic field is applied, while it tends to saturation if the field is relatively high [80, 81].

Figure 2.2. Microstructures of (a) isotropic and (b) anisotropic magnetic elastomers [82].

As a representative of soft active materials, magnetic elastomers possess two remarkable features, namely it deforms and changes its elasticity simultaneously [83] under external magnetic field. The magnetic field-induced deformation is commonly known as magnetostriction, and the changeable stiffness by a magnetic field is referred to as magnetorheological (MR) effect [80].

2.1.1. Magnetostriction

Magnetostriction was initially identified by James Joule in 1842 when observing the motion of iron under a uniform magnetic field [84]. Subsequently, it was demonstrated in ferromagnetic metals, alloys, and elastomers [85, 86], and found that magnetostriction in magnetic elastomer is about thousand times larger than that in metals and alloys [87], due to its soft nature. For example, a strain of 1.4% was measured in a magnetic elastomer under the magnetic intensity of 120 kA/m [64], while only 0.001% saturation magnetostriction obtained in alloys under the same intensity [87].

The mechanism of magnetostriction may be attributed to the magnetic force created by a uniform magnetic field. Without an external magnetic field, the magnetic moment of any particle is kept along its easy-axis and randomly distributed, as shown in Figure 2.3(a). Hence, the macroscopic magnetization is zero and no particle-particle interaction occurs. However, if an external field is imposed, the magnetic elastomer may be magnetized through two different procedures. Each particle alters the magnetic moment direction without rotating its body, as illustrated in Figure 2.3(b), and each particle physically rotates itself against the matrix to approach the field direction, while retains its magnetization along the easy-axis, as shown in Figure 2.3(c). In multicrystalline ferromagnetic material, the first process may be dominant. However, both processes may occur concurrently in a magnetic elastomer with relatively soft matrix [43]. Once magnetized, the particle-particle interactions are initiated and the particles may attract or repel each other. Since the particles are attached tightly onto the polymer chains, the movements of particles result in an overall macroscopic deformation in elastomer.

Figure 2.3. Schematic of the elastomer magnetization. (a) Magnetic moments of the magnetic particles are randomly dispersed in the polymer matrix; (b) The magnetic particles change their magnetization directions without rotating their spatial position; (c) Particles maintain their magnetization along easy-axis, while physically rotate against the matrix along the field direction.

On the other hand, magnetic force may also be generated by a nonuniform magnetic field, where the particles in the polymer matrix experience a magnetophoretic effect and are attracted to the region with higher field gradient. Recently various deformation patterns were experimentally performed, such as elongation and contraction [24, 88], bending [89, 90], coiling [91], and deflection [92]. It is found that magnetostriction induced by a nonuniform magnetic field is much pronounced than that caused by a uniform field. For example, an elongation strain of around 40% was reported through applying a nonuniform magnetic field [3], while only a strain of several percentages was observed under a uniform field [64]. Apart from the static response, the dynamic behavior of the magnetic elastomer was also investigated, where the elastomer underwent a sinusoidal motion with its deformation frequency doubled that of the applied field [93], if a cyclic magnetic field was imposed.

Figure 2.4. Phenomena of instability and hysteresis under a nonuniform magnetic field.

Magnetic elastomer may exhibit the phenomena of instability and hysteresis under a nonuniform magnetic field. For instance, significant deflections occur if the magnetic field applied exceeds a certain value [92]. Elastomers may elongate linearly at a low magnetic field, while a very large and abrupt elongation occurs if the field increases at a certain value, as illustrated in Figure 2.4. Afterwards, no noticeable change in elongation is found if the magnetic field increases further, which is followed by a saturated strain. Similarly to the elongation, an abrupt contraction is also observed with decreasing magnetic field. Furthermore, the contraction path does not follow that of the elongation path, which is referred to as the phenomenon of hysteresis. It is worth mentioning that the hysteresis process is not the consequence of magnetic hysteresis of ferromagnetic particles, since the particles are filled at micro- or nano-level and show paramagnetism [94, 95]. Apart from the external magnetic field, geometrical parameters, including specimen length, aspect ratio, and elastomer-magnet distance, were also demonstrated to have significant impacts on magnetoelastic instability of the elastomers [75, 96].

Recently the phenomena of instability and hysteresis were widely investigated to facilitate their application for a variety of areas, including transducers and actuators [92].

2.1.2. Magnetorheological effect

The Magnetorheological (MR) effect, also known as temporary reinforcement in stiffness, is constructed or vanished if the external magnetic stimulus is imposed or removed [58]. It was initially observed in MRF whose yield stress and viscosity were changed from a Newtonian liquid to a non-Newtonian liquid when exposed to a uniform magnetic field [53, 97]. Experimental works showed that both the shear and tensile modulus of the magnetic elastomer increase under a magnetic field, as illustrated in Figure 2.5. The mechanism of MR effect may be attributed to the additive of magnetization energy into the magnetoelastic system to induce the particle-particle interactions [58], resulting in internal forces to increase the effective stiffness of the magnetic elastomer. Apart from the applied magnetic field, the MR effect was also related to the particle shape, concentration, and size distribution [53, 62].

Figure 2.5. MR effect on (a) the shear modulus [78], and (b) the tensile modulus [80].

MR effects are much different on isotropic and anisotropic magnetic elastomers. For isotropic magnetic elastomer, only several percentages of increase in elastic modulus were observed [58]. In order to enhance the magnetic reinforcement effect, the anisotropic elastomer was prepared by varying the spatial distribution of the particles, and it demonstrated that the MR effect is much more prominent on the uniaxial field structured elastomer than that with random particle distribution [58]. Furthermore, the temporary reinforcement was the most pronounced if the external magnetic field is along the direction of the particle chains [58, 65].

2.2. Experimental investigation on magnetic hydrogel

2.2.1. Magnetic-sensitive hydrogel

As a novel smart material, magnetic-sensitive hydrogel is composed of a soft polymeric matrix, in which water and magnetic particles are filled at micro- or nano-level [22, 24]. Subject to an externally imposed magnetic field, the magnetic hydrogel undergoes a finite deformation. Recently the magnetic-sensitive hydrogel attracts considerable attention due to its unique characteristics, including the fast response, low friction, biocompatibility, and remote actuation [98]. Therefore, the magnetic hydrogel is adopted widely in diverse areas, including chemical adsorbent [27], drug delivery [29], and microfluidic valve [28].

To provide the guidance for design and optimization of the magnetic-sensitive hydrogel, increasing interests were attracted on coupling behaviors of the magnetic hydrogel in past decades. Ateyyah *et al.* [99] explored the influence of external magnetic field on swelling ratio of a PMAA-based magnetic hydrogel immersed in pure water, and showed that the hydrogel swelling was significantly associated with the magnetic

intensity and the concentration of nanoparticles, and the diffusion coefficient of solvent decreased exponentially with increasing magnetic intensity. In another work [48], hydrogels were incorporated with isotropically and anisotropically dispersed magnetic particles respectively, where the isotropic hydrogel elongated along the magnetic field direction and contracted in the transverse direction, while the anisotropic one revealed the opposite responsive behavior. For investigation of the swelling behavior of a polyelectrolyte magnetic hydrogel subject to a uniform magnetic field, Safronov *et al.* [59] prepared the magnetic hydrogel by combination of the copolymer of acrylamide and potassium acrylate, where a positive magnetostriction was observed if the particle filling ratio was relatively low, and negative magnetostriction found when the filling ratio was high.

Recently the increasing attentions were received on development of magnetic-sensitive hydrogel-based device, such as microfluidic flow controller, which is employed to generate desired flow patterns in real-time for replicating various physiological and pathological conditions in the human. The early flow controller in microfluidics mainly opted the flexible membranes [100] and external pressure pump [101] to handle and control the flow, while its application is impeded due to the sophisticated system configuration and high cost of the supporting equipment. Alternatively, the stimuli-sensitive hydrogel is employed as the microfluidic flow controller due to its simple system configuration, since it eliminates the necessity for integrated electronics, controls, and power source, which are required for conventional microfluidic device [102-104]. So far numerous stimuli-responsive hydrogels have been used in microfluidics, where the pH-sensitive hydrogel may be the most common one as the sensor or actuator for flow

control [18]. However, the hydrogel is required to contact the surrounding solution with the specific pH [104, 105], which may restrict the development of the microfluidic system in analytical instrument at remote locations [106]. In addition, the time response of the single pH-sensitive hydrogel was relatively slow [4, 18, 102]. Although two strategies were proposed to improve the response rate, such as utilization of the macroporous hydrogel or multiple smaller hydrogel disks, the hydrogel suffers from low mechanical stiffness [4, 14, 107], making it inappropriate for dynamic control of the microfluidic flow with a wide range of patterns required by the microphysiological systems. Therefore, much effort was made to investigate the magnetic-sensitive hydrogel as microfluidic controller [108-111]. An important advantage of the magnetic hydrogel over pH actuated controller is that the hydrogel behavior can be controlled from outside the device [104], without direct contact with the external magnetic stimulus. Furthermore, the magnetic hydrogel responds fast to the external magnetic field, which is crucial for a microfluidic flow manipulation [106].

Another promising application in biomedicine is the magnetic-sensitive hydrogel-based targeting system for drug delivery. As is commonly known, magnetic field does not require special environmental properties such as conductivity and transparency, and it is biocompatible to the human body even at relatively high field strength [105]. Furthermore, it enables to manipulate the magnetic objects toward the specific organ or tissues of the body [112-114], resulting in increased drug concentration at the target tissue with low systematic toxicity. In general, the magnetic drug carrier is developed by adding highly permeable magnetic nanoparticles into a non-magnetic matrix [115-117], where usually the hydrophilic polymer is adopted [115, 117-119], due to its capability to

enhance the water solubility of hydrophobic drugs, extend the circulation of drugs in blood, and suppress or eliminate fast renal excretion. A literature review reveals that so far various experimental works have been conducted to characterize the performance of the magnetic-sensitive hydrogel-based drug targeting system. Chen *et al.* [120] synthesized the polyvinylpyrrolidone magnetic hydrogel microsphere loaded with the chemotherapeutic drug and then the microsphere was guided to the tumor site by an external magnet. After two weeks, the drugs were mostly accumulated at tumor site and the tumor size was reduced significantly. Effective magnetic drug targeting was also revealed by Sun *et al.* [117] when they injected magnetic polyacrylamide hydrogels into rabbits, and found that the drugs were mainly retained at the right back leg of the rabbit, where the permanent magnet was positioned. In order to improve the antitumor efficacy of intravesical Bacillus Calmette-Guérin, the drug-loaded magnetic chitosan hydrogel was prepared by Zhang *et al.*, [121] and it was attracted and attached to the bladder wall by an external magnetic field. After two days, the tumor number decreased about five times compared with that of the traditional therapy. Recently the multi-stimuli-responsive hydrogels were developed for efficient synergistic therapy, such as the simultaneous drug targeting and release, where the magnetic nanoparticle were generally embedded for site-specific targeting, and the pH- [116, 122], temperature- [123, 124], or light-sensitive [125] functional groups incorporated for drug release at desired rate.

2.2.2. Magnetic-pH-sensitive hydrogel

Solution pH is a common stimulus of environmental-responsive hydrogels. In general, the pH-sensitive hydrogel contains pendant charged groups that combine/decompose protons when the environmental pH level changes, such as acrylic acidic and carboxylic.

The hydrogel with ionic groups is also referred to as polyelectrolyte hydrogel [13]. For applications in most cases, hydrogels are required to respond fast to the environmental changes. However, it is a limiting factor for the conventional pH-sensitive hydrogels. To address the challenges related to efficacy of the smart material, the dual magnetic- and pH-responsive hydrogels were developed by immobilization of the magnetic particles into the polymeric chain through hydrogen bonding [66], coordination bonds [67], electrostatic attraction [68], or covalent attachment [25]. Due to the dual and rapid response characteristics, magnetic-pH-sensitive hydrogels were used in diverse areas including heavy ions adsorption [126], drug delivery [127], and catalysis [128]. The hydrogels were also employed as pH chemical sensor, since the magnetic permeability of the hydrogel varies with the hydrogel deformation in response to solution pH [74, 129]. Furthermore, the dual magnetic-pH-sensitive hydrogel-based scaffold was synthesized and characterized to provide appropriate cell microenvironment for efficient tissue promotion by delivering various biophysical and biochemical cues, when subjected to magnetic and pH coupled stimuli [50, 130].

The application of the magnetic-pH-sensitive hydrogel lies in a thorough understanding of the responsive mechanism. If the hydrogel is placed in bath solution, some functional groups dissociate and it then results in the formations of the mobile ions and fixed charges attached to the chain. Due to the fixed charges, the ionic concentration within the hydrogel differs from that in the solution. Consequently, an osmotic pressure is generated and it contributes to the swelling or deswelling of the hydrogel. Simultaneously, if an external magnetic field is employed, two distinct interactions may occur, particle-particle and field-particle interactions, due to the magnetic particle

magnetization and the magnetic field gradient respectively [131]. Since the particles are tightly anchored into the flexible network chain, the movement of the particles further drives the deformation of the hydrogel [90], which in turn redistributes the magnetic field, diffusive mobile ions, as well as fixed charge groups, and thus induces new ionic concentration differences to deform the hydrogel again. The recurrent kinetics cease until an equilibrium state is reached.

2.2.3. Magnetic-temperature-sensitive hydrogel

Experimental works on remote heating of magnetic materials may date back to 1957 when Gilchrist *et al.* [132] heated various tissue samples embedded with magnetic nanoparticles ranging from 20 to 100 nm, by an alternating magnetic field (AMF) with a frequency of 1.2 MHz. After that, many heat agents were emerged such as PdNi, duplex stainless steel, amorphous metal flakes, gold, carbon nanotubes, clay, and ceramic [133-135]. However, all these materials are invasive and required careful surgery for *in vivo* applications [136]. As hydrogels are proved to be biocompatible and the thermal behavior of the magnetic particles can be remotely controlled, the combination of hydrogels with magnetic particles becomes the reasonable choice for biomedical applications.

In recent year, continuous efforts have been done to incorporate the magnetic particles into temperature-sensitive hydrogels. The hybrid hydrogels exhibit peculiar dual-responsive properties with the capability of remote actuation by external AMF. In magnetic-temperature-sensitive hydrogels, magnetic particles are employed as the heat source. Under the AMF with high frequency, the magnetic particles can be heated and then transferred to the bulk hydrogel. If the temperature within the hydrogel exceeds its

volume phase transition temperature, for example about 35°C for the NIPAAm hydrogel, the hydrogel may be collapsed with a sharp decrease of the swelling ratio. The noticeable characteristics of magnetic hydrogel were widely used in remotely controlled drug release systems [137-143], as illustrated in Figure 2.6. The initial work of using magnetic hydrogels for thermo-magnetically activated drug release was conducted by Hoffman *et al.* [144], where the evenly distributed drugs inside the matrix were squeezed out of the system due to the hydrogel deswelling induced by the increasing environmental temperature above the critical volume phase transition temperature. Sousa *et al.* [42] synthesized a dual-functional (SBA-15/Fe₃O₄/PNIPAAm) hybrid system and showed that the release rate was enhanced from about 40% to 70% if the AMF was applied. Mengesha *et al.* [139] reported a 61% increase in release amount compared with the conventional release method. Liu *et al.* [145] revealed a highly controllable and repeatable burst release. By an on-off switching mode, Hayashi *et al.* [138] effectively controlled the release rate.

Figure 2.6. Schematic of the remote-controlled drug release system [143].

Magnetic-temperature-sensitive hydrogel was also good candidate as microfluidic valve [104], as shown in Figure 2.7. The valve was integrated into a ceramic microfluidic device with Y-junction channels, and then an AMF with frequency of 293 kHz was imposed for ON-OFF control on the fluid flow. In contrast to the pH-actuated valves which are required to contact with the controlling solution, the magnetic-temperature-hydrogel-based valve is free of contact and can be remotely controlled. Although the response of the valve is in minute scale, its performance can be remotely and precisely controlled via magnetic field outside, making the hydrogel very attractive as actuators in micro-devices.

Figure 2.7. Schematic of remote control of the magnetic valve system [104].

2.2.4. Other magnetic hydrogels

Apart from the single response hydrogel (e.g. magnetic-sensitive hydrogel) and the common dual response hydrogel (e.g. magnetic-pH-sensitive hydrogel or magnetic-

temperature-sensitive hydrogel), other multiple responsive magnetic hydrogels were developed for diverse applications. Wang *et al.* [146] designed and prepared a magnetic-light-sensitive hydrogel-based actuator by combination of hydrogel with the magnetic particles and the near-infrared light-sensitive graphene oxide. It enables to accomplish the comprehensive actuation of “extension-grasp-retraction” like a fishing rod, with the excellent properties of rapid response and strong mechanical strength. Fusco *et al.* [125] presented a magnetic-pH-light-sensitive hydrogel as an integrated microrobotic platform for targeted therapeutic interventions. In addition, the magnetic-pH-temperature-sensitive hydrogel was fabricated and showed that the swelling ratio in the presence of AMF is higher than that without magnetic effect [147].

2.3. Theoretical models for polymer-based materials

2.3.1. Magnetic elastomer

A literature review reveals that modeling of the magnetic elastomers may be categorized by different length scales. At the macroscopic level, the magnetic composites are considered as continua, and the elastomer is assumed to be incompressible with constant volume [88]. At the mesoscopic level, usually the polymeric matrix was regarded as an elastic continuum and the discrete magnetic particle regarded as a dipole, such that the influences of the particle concentration and its spatial distribution were investigated on the magnetic elastomers [148-152]. In order to capture more details at microscopic scale, including structure of the polymer and coupling of individual polymer chain with the magnetic particles, the microscopic models were developed in 2D and 3D dimensions [44, 153].

2.3.1.1. At macroscopic level

Early macroscopic models by Zrúnyi group [24, 65, 88, 90, 94, 95, 154, 155] tended to compute the magnetic field separately and then added the magnetic effect into the mechanical equilibrium equation. Initially their theoretical model focused on unidirectional elongation and contraction in a nonuniform magnetic field, which concluded that the elongation at small strains was proportional to the square of magnetic intensity due to the current intensity applied [24, 88]. Subsequently, their research works were extended to predict various deformation patterns such as bending, rotation, or combination of both deformations [90, 154]. Furthermore, a macroscopic magneto-mechanical model was formulated to describe the kinetics of the shape change based on retarded elasticity and lumped inertia [154]. On the basis of the theoretical works by Zrúnyi group, Ramanujan *et al.* [96] developed an energetic model analogous to phase transformation for the phenomena of instability and hysteresis during elastomer deformation, and also formulated a finite element model for the coiling behavior [91]. Apart from nonuniform magnetic fields, several theoretical models were also developed to study the magnetostriction induced by uniform magnetic field, where the Maxwell equations were coupled with the linear elasticity [156-160]. In addition, a complete set of continuum dynamic theory was formulated by the hydrodynamics concept for isotropic ferrogels [161] and uniaxial magnetic gels [162]. According to the energy approach by Landau *et al.* [163], Morozov *et al.* [164] investigated two competitive mechanisms, magnetostatic and magnetostrictive, that determine the final type of the deformation, either elongation or contraction. The former results from the change of demagnetizing

field associated with initial geometric shape, and the latter relates to the change of magnetic permeability associated with elastomer deformation.

For modeling of the responsive behavior of magnetic elastomers with nonlinear elasticity, instead of the infinitesimal deformation, historically two continuum-mechanics approaches were mostly adopted: (i) based on direct approach, where the conservation laws of continuum mechanics were employed for the constitutive equations [165-168]; and (ii) based on energy approach, where the calculus of variations were used to minimize an appropriate potential energy [169, 170]. It is shown that both methods give rise to the same set of governing and constitutive equations [170].

A pioneering work with direct approach for electromagnetism and deformed media was reviewed by Pao [165], which was widely used as the main source of references for many subsequent researchers in the theory of magneto-mechanical coupling on soft ferromagnetic solids. In parallel, based on the invariance principles and the matrix polynomials, Jordan and Eringen [171] developed a constitutive theory for steady-state response of an elastic solid in response to the mechanical, thermal, electromagnetic coupled fields. The work provided a complete form for the magneto-elastic theory, with governing equations of the Maxwell equations, as well as the conservations of mass, momentum, and energy. However, some of the derived parameters, such as the stress tensor, had more than 100 unknown components, which impedes the theory from being further developed.

Following the work of Pao [165], a fully coupled nonlinear field theory was developed for isotropic magnetic elastomer by Dorfmann and Ogden [172-177], where

the Maxwell's equations were coupled with the nonlinear elasticity, and the constitutive equations were achieved by the second law of thermodynamics. In addition, some boundary value problems were solved, including the shear of a slab [176], helical shear [174], the extension and torsion of a circular cylinder [174], as well as the steady rotation of a tube [178]. In addition, the theory of Dorfmann and Ogden was extended for anisotropic magnetic elastomer through including additional four invariants related to particle alignment direction [179]. Furthermore, two boundary value problems were investigated such as the extension and inflation of a circular cylindrical tube, and the extension and torsion of a solid circular cylinder [179].

Concurrently with the direct approach, the energy-based method was also used to derive the governing equations for magnetoelasticity on soft electromagnetic material. Brown [180] used the constrained minimization method to achieve the governing equations in an approach analogous to Toupin's variational treatment of an elastic dielectric [181]. Subsequently, Kankanala and Triantafyllidas [170] developed a new coupled variational formulation with respect to Lagrangian coordinate for magnetoelasticity with finite strain. By minimizing the potential energy regarding its independent variables, all the governing equations were achieved, and then two boundary value problems were studied, including uniaxial traction and torsion of cylinders under external magnetic field.

For characterization of the performance of the magnetic elastomer, the specified free energy functions are needed, where the principle invariants are often adopted as the independent variables. Danas *et al.* [182] proposed a transversely isotropic energy density

function which depends on two mechanical and five magnetoelastic invariants. The formulas were capable of accurately predicting the initial magnetization slope, initial magnetostriction curvature, and magnetization saturation of the magnetic elastomer. Dorfmann *et al.* [176] constructed a specific energy function for incompressible isotropic magnetoelastic material, and the energy function can be reduced to the classical neo-Hookean strain energy when external magnetic field is absent. For a compressible isotropic material, Bustamante *et al.* [183] developed an isotropic free energy function with six invariants, where the function was decomposed into three parts, namely isochoric, volumetric, and adjustable parameter.

It is known that the magnetic field distribution and field-induced deformation are the key factors for design of the magnetic elastomer-based device such as microactuator in MEMS. A literature search reveals that usually the uniform magnetic field and deformation are considered in the developed magneto-mechanical model to simplify the theoretical analysis, where the elastomer with infinite geometric size is employed and the computational domain merely covered the elastomer, i.e. the influences of the surrounding and interface were neglected [174, 184]. However, a transition may occur from the uniform to nonuniform magnetic fields, if the magnetic elastomer is varied geometrically from the infinite to finite size, and vice versa. As well known, owing to the different magnetic permeabilities between the elastomer and its surrounding, the uniform magnetic field applied is perturbed to a nonuniform one after the finite elastomer is placed into the field. The resultant nonuniform field induces the inhomogeneous deformation of the elastomer, and then the deformation makes the magnetic field redistributed further until an equilibrium state is reached. If the magnetic elastomer is

changed geometrically from finite to infinite size, the nonuniform magnetic field is then altered to the uniform one again [47]. A literature study shows that so far no effort has been made on the transition phenomenon between the uniform and nonuniform magnetic fields due to the elastomer geometric size, and most of the theoretical studies were done on modeling of the uniform magnetic field only, in which the infinite magnetic elastomer was placed [174, 184]. However, usually the finite elastomer was used in the experiment, where the surrounding and the interface may play important roles in its responsive behavior. Consequently, a remarkable discrepancy was found between the model prediction and experimental result [46, 47]. The inconsistency remains unclear, probably due to lack of a robust model for determining the magnetic field transition that is associated with the magnetic elastomer geometry.

2.3.1.2. At mesoscopic level

The merits of the macroscopic continuum-mechanics approaches are the relative simplification of the modeling process and the possibility to reach long length and time scales [44], while the discrete material properties are not taken into accounts, such as particle size, shape, and its arrangement [149]. However, these details may influence significantly on macroscopic magnetoelastic response of the magnetic elastomer [44], such that several microstructure-based magneto-mechanical models are developed at the mesoscopic level, where the polymeric matrix was regarded as an elastic continuum and the discrete magnetic particle taken as a dipole.

The most conventional mesoscopic model for magnetic elastomer may be based on the magnetic dipole-dipole interaction between two adjacent particles [78], in which two

assumptions are mostly employed [149], (i) the particles are considered as dipoles due to its relatively small size, and (ii) the dipoles possess the equivalent magnetic moments. Under these assumptions, the magnetostatic energy with respect to the interaction between two adjacent dipoles is defined as a function of the dipole-dipole distance, the dipole moment, as well as the angle between the field direction and the line linking the two dipoles [78]. If no external constraints exist, stress vanishes in the equilibrium state and the magnetostrictive strain is calculated. The increases in shear and Young's modulus are achieved through the second derivation of magnetostatic energy with respect to the shear and tensile strain respectively [149].

The simple magnetic dipole model enables to characterize the magnetic field-induced deformation [185], and recover the MR effect in shear, while it is unable to explain the MR effect in tension/compression [45]. Because it always predicts a decreasing tensile stiffness [149], which is in contrast to the experimental finding [80]. The inconsistency may result from the incorrect microstructure description, e.g. the straight particle chain within the elastomer. Thereby, Han *et al.* [45] developed another microstructure-based model with consideration of the wavy-chain structure to elucidate the relationship between the tensile modulus and the magnetic field applied. In addition, other responsive mechanisms were considered in the model including chain-chain interaction and non-affine deformation, and it was concluded that the magnetic interaction between particles is the major cause of the MR effect, compared with the other effects of chain-chain interaction and non-affine deformation.

Usually magnetic elastomer with infinite size is considered in the mesoscopic models mentioned above, such that the effect of elastomer geometry is neglected. To address the issue, Zubarev [151, 152, 186, 187] qualitatively predict deformation of the ellipsoid elastomer with finite size, by the standard methods of statistical physics. It demonstrated that the sign of deformation along the field direction, either elongation or contraction, is highly dependent on the initial shape of the magnetic sample, the applied magnetic field, as well as the particle concentration. In another work, Ivaneyko *et al.* [188] combined macroscopic continuum-mechanics and microscopic approaches for elastomers with different shapes and particle arrangements, which was successfully to predict the magnetic field inside the elastomer, and the signs of the deformation and the change of elastic modulus.

2.3.1.3. *At microscopic level*

To account for more details at microscopic scale, the 2D and 3D dipole-spring models were developed with consideration of the magnetic particles with individual polymer chain of the surrounding elastic matrix, by molecular dynamics simulations via ESPResSo software [44, 153], in which two distinct microscopic simulations were conducted in detail. The first simulation is based on so-called Néel mechanism, in which the magnetic moment rotates while the nanoparticles remain unmoved under external magnetic field. Under this mechanism, the magnetic elastomer elongates with the field line while shrinks in the perpendicular direction. The second simulation is based on the so-called Brownian mechanism, where the magnetic torque exerted on the nanoparticle is transferred to the polymer chains, resulting in a macroscopic shape change. Raikher *et al.* [189] studied the evolution of the particle chain by coarse-grained molecular dynamics

simulation with consideration of uniaxial magnetic anisotropy. To investigate the conformation of flexible magnetic filaments, Sanchez *et al.* [190] formulated a bead-spring chain model by means of Langevin dynamics simulation.

Apart from the deformation, the elastic property of the magnetic elastomer in uniform magnetic field was also studied by microscopic model and Monte Carlo simulation [191], showing that the elastomer elastic moduli can be tailored by different magnetic fields applied during gel-formation stage. Furthermore, the scale-bridging approach was proposed to bridge across multiple scales from the microscopic to macroscopic scales [192, 193].

2.3.2. Non-magnetic hydrogel

With the increasing hydrogel applications, hydrogels with more complicated shapes and control methods are required. In addition, the accurate estimate of hydrogel response under external stimuli is not convenient by experiments. It is thus critical to predict the behavior of hydrogels by the development of mathematical models for getting an insight into the fundamental mechanisms of hydrogels. Significant progress in numerical prediction was achieved for the past few years. Among them, the transport model, mixture theory, and thermodynamic models are mostly employed.

2.3.2.1. Transport model

In transport model, the volume transition of swelling is diffusion-driven [194]. The models developed are commonly based on the conservations of mass and momentum. A representative theoretical frame consists of the Nernst-Planck equation, the Poisson equation, as well as the equation of mechanical balance. By the set of nonlinear coupled

equations, together with the corresponding constitutive equations, the deformation behavior of hydrogels are predicted. The transport model simplifies the interactions within the hydrogel system and provides both transient and equilibrium swelling behavior for ionic hydrogels [195-197]. The model enables to predict both the ion concentration and the electric potential over the domains covering hydrogel and surrounding solution, and the stress within hydrogel. Moreover, It is employed to explain the bending behavior of ionic hydrogel under electric stimulus [195]. However, the transport model ignores the friction forces among polymer chain, solvent, and ions that may otherwise have crucial effects on hydrogel performance. Furthermore, this model may only be applied for certain hydrogels where deformation mainly results from ionic diffusion. For neutral hydrogels, this model may not be able to give an accurate prediction.

2.3.2.2. *Multiphasic model*

In mixture theory, hydrogels are separated into three phases: solid, water, and ionic phase with both anions and cations [198]. The hydrogel volume transition is driven by the forces associated with the gradient of chemical or electrochemical potentials, which are balanced by frictional forces in hydrogel [194]. In this model, the three phases are assumed intrinsically incompressible, while the whole hydrogel is compressible by exudation of water.

The multiphasic model enables to predict the transient and equilibrium behavior of neutral hydrogels and polyelectrolyte hydrogels under various solvent, electric, and mechanical stimuli. It was used to investigate the swelling, shrinking, and bending behaviors of electric-sensitive hydrogel subject to external electric fields [15], and also

employed to study the response of soft tissues under compression and indentation [199], since the constitution of hydrogel is similar to the biological tissue.

The mixture theory simplifies the interactions among the water, mobile ion, and the polymer chains, and it does not consider the variation of hydrogel elastic properties during its swelling process. In addition, it assumes constant frictional coefficients among each phase.

2.3.2.3. *Thermodynamic model*

Thermodynamic model provides a simple way to describe swelling of the neutral and polyelectrolyte hydrogel. The volume transition in the equilibrium state is obtained if the solvent within the hydrogels is in thermodynamic equilibrium with the external solvent. This equilibrium can be described by free energy, chemical potential or the related osmotic pressure [194].

On the basis of the field theory of poroelasticity by Biot [200], Suo *et al.* [200, 201] formulated a theory that couples large hydrogel deformation and solvent diffusion. When hydrogel is immersed in water, small molecules diffuse into the polymer network, resulting in the expansion of the polymer chains. In this theory, two modes of deformation are assumed within the hydrogel system. The first mode results from local rearrangements of water molecules, allowing the hydrogel to change its shape not volume. The timescale of this mode is independent of hydrogel size. For the second mode, namely the long-term mode, is caused by migration of water molecules into polymer matrix, allowing the hydrogel to change both the volume and shape. As the first mode corresponding to polymer chain rearrangement is much faster than the second

diffusion dominating mode, it is assumed that the first mode is instantaneous whereas the second mode is time-dependent. In thermodynamic model, the individual polymer and water molecules are assumed to be incompressible. In other words, the volume of the hydrogel is the sum of molecule volume and dry polymer volume.

The thermodynamic model is able to simulate and analyze both the equilibrium and transient behavior of hydrogels. It was used to study the inhomogeneous swelling of hydrogel under various external solvent and mechanical loads. Swelling-induced bifurcation was also studied extensively [202]. The model was also implemented to capture the evolution of stress fields at the crack tip [203]. Moreover, FEM simulation of creases formed in a thin hydrogel was also conducted [204].

The theoretical framework of the thermodynamic model is open, allowing any energy form to be inserted, such as polarizing energy [201], and dissociation energy [205]. Therefore, it can be applied to diverse hydrogels as long as the free energy function is specified. With regard to the corresponding kinetics laws for the swelling process, it assumes that self-diffusion of water molecules dominates the kinetic process. The assumption may not be accurate if macroscopic flow or convection of solvent molecules prevails in the hydrogels.

2.3.3. Magnetic hydrogel

Despite many experiments over the past years, few of them concentrated on the mathematical modeling of the magnetic-sensitive hydrogel placed in solvent surrounding subject to external imposed magnetic field. A literature search reveals that that so far only one theoretical work for a magnetic-sensitive hydrogel immersed in a solvent, subjected

to a uniform magnetic field in the equilibrium state, has been published to predict the swelling via its volume fraction ratio only [30], meaning that the present hydrogel swelling deformation is a scalar, instead of a vector. Thereby, it is unable to characterize the deformation behavior of the magnetic hydrogel appropriately. Recently relevant experimental works were conducted for the deformable magnetic hydrogel. However, the results seem to be contradictory to each other qualitatively. For example, some of them showed that the hydrogel in a uniform magnetic field elongated along the field direction and contracted in the transverse direction [48, 49], while another experiment demonstrated a contraction in the field direction [50]. The contradiction remains unclear, probably due to the lack of an efficient model to characterize the fundamental mechanism of the performance of the magnetic-sensitive hydrogel. Regarding the dual magnetic-pH-sensitive hydrogels, a further literature survey shows that so far no effort has been done in theoretical work for the dual responsive hydrogel. In order to facilitate the utilization of magnetic hydrogel, it is vital to characterize the responsive mechanism of the magnetic hydrogel with multi-field coupled effects by a multiphysics model.

2.4. Remarks

The chapter reviews the experimental and theoretical works on magnetic elastomers and hydrogels in the literature. In accordance with the present literature review, three conclusions on modeling of the magnetic elastomers and hydrogels are highlighted and presented below.

- Despite numerous models at different length scales for the magnetic elastomer, the uniform magnetic field and field-induced deformation are often considered to simplify the theoretical analysis, where the elastomer with infinite geometric size is

employed and the computational domain merely covered the elastomer, i.e. the influences of the surrounding and interface were neglected. However, usually the elastomer with finite size was used in the experiment, where the surrounding and the interface may play important roles in its responsive behavior. Consequently, a significant discrepancy was found between the model prediction and experimental result [46, 47].

- For modeling of the magnetic-sensitive hydrogel, apart from magneto-mechanical coupled effects considered in magnetic elastomer, the chemical field is required due to solvent diffusion in hydrogel system. The literature survey reveals that so far only one theoretical work for a magnetic-sensitive hydrogel immersed in a solvent, subjected to a uniform magnetic field in the equilibrium state, has been published to predict the swelling via its volume fraction ratio only [30], meaning that the present hydrogel swelling deformation is a scalar, instead of a vector. Therefore, it is unable to describe the deformation behavior of the magnetic hydrogel appropriately.
- Regarding the theoretical work on the dual magnetic-pH-sensitive hydrogel, the responsive mechanisms of the ionic diffusion and polarization are required to be considered, in addition to the solvent diffusion, hydrogel magnetization, and nonlinear deformation within the magnetic-sensitive hydrogel. The literature review shows that so far no effort has been made in theoretical modeling for the dual magnetic-pH-sensitive hydrogel.

Chapter 3. Development of a Multi-Effect-Coupling Magnetic-Stimulus (MECm) Model for Magnetic-Sensitive Hydrogel

3.1. Introduction

In this chapter, a 3D multi-effect-coupling magnetic-stimulus (MECm) model is developed for simulation of the responsive behavior of the magnetic-sensitive hydrogel, with the effects of magneto-chemo-mechanical coupled fields. The MECm model is reduced to simulate and analyze the magnetic hydrogel response in the equilibrium state. It is then extended by considering moving fluid instead of still fluid, where the transient fluid-structure interaction is characterized between the deformable magnetic hydrogel and surrounding fluid flow by the fully coupled arbitrary Lagrangian-Eulerian (ALE) algorithm. This chapter is organized as follows. After this section, several assumptions are made and presented in Section 3.2. Section 3.3 formulates the governing equations for the conservations of mass, momentum, as well as hydrogel magnetization, and then derives the constitutive relations by the second law of thermodynamics. The reduction of the MECm model in the equilibrium state is presented in Section 3.4, followed by its extension with consideration of moving fluid formulated in Section 3.5. After that, Section 3.6 elaborates the validations of the MECm model with several theoretical and experimental data in open literature. Finally, several remarks are given in Section 3.7.

3.2. Assumptions

The following assumptions are made for the present theoretical work, unless otherwise stated.

- The magnetic particles are immobilized and distributed homogeneously within the hydrogel.
- The hydrogel has the macroporous property, thus the diffusivity constant of the solvent molecules remains the same in both the hydrogel and surrounding solvent.
- The externally applied magnetic field is not perturbed, such that the direction of the magnetic field is unchanged in the hydrogel system. In general, the magnetic field may be perturbed due to the different magnetic permeabilities between the hydrogel and the surrounding solvent. However, in the MECm model in the equilibrium state, the magnetic field line is not distorted, since the size of magnetic hydrogel is much smaller than that of the electromagnet, and the permeability of the hydrogel is relatively small [80]. In the transient extended MECm model however, the change of the magnetic field direction is considered to achieve an accurate distribution of magnetic field.

3.3. Formulation of the MECm model

In this section, a 3D multiphysics model is developed by coupling the magnetic, chemical, and mechanical effects together, where the nonlinear finite deformation is allowed.

3.3.1. Kinematics

In general, for a magnetic hydrogel initially undeformed in the absence of external mechanical force or magnetic field, the volume of the magnetic hydrogel may be defined as V_0 enclosed by a boundary S_0 in a reference configuration, with material point labeled by the position vector $\mathbf{X} \in V_0 \cup S_0$. By the nonlinear elasticity theory [206], if the

material point $\mathbf{X}$ moves to the spatial point $\mathbf{x}(\mathbf{X}, t) \in V \cup S$, the deformation gradient $\mathbf{F}$ is defined as

$$\mathbf{F} = \nabla_{\mathbf{x}} \mathbf{x} = \frac{\partial \mathbf{x}}{\partial \mathbf{X}} \quad (3.1)$$

where $\nabla_{\mathbf{x}}(\bullet)$ denotes the material gradient operator with respect to $\mathbf{X}$. The Jacobian of the transformation is given by the determinant $J = \det(\mathbf{F})$ with the standard convention $J > 0$.

3.3.2. Magnetostatics

In the absence of free current and time-dependence effect, the magnetostatic field is governed by the classical Maxwell's equations as [176]

$$\text{Ampere's law: } \nabla \times \mathbf{h} = 0 \quad (3.2)$$

$$\text{Gauss's law: } \nabla \cdot \mathbf{b} = 0 \quad (3.3)$$

where $\nabla \times (\bullet)$ and $\nabla \cdot (\bullet)$ denote the spatial curl and divergence operators with respect to $\mathbf{x}$, respectively. Vectors $\mathbf{b}$ and $\mathbf{h}$ are the magnetic induction and intensity respectively with respect to $\mathbf{x}$, formulated by the following relation

$$\mathbf{b} = \mu_0(\mathbf{h} + \mathbf{m}) \quad (3.4)$$

where $\mathbf{m}$ is the magnetization vector and μ_0 the magnetic permeability in a vacuum.

Across the interface between the magnetic hydrogel and surrounding solvent, the magnetic induction $\mathbf{b}$ and intensity $\mathbf{h}$ are required to satisfy the following jump conditions [176]

$$\mathbf{n} \cdot [[\mathbf{b}]] = 0, \quad \mathbf{n} \times [[\mathbf{h}]] = 0 \quad (3.5)$$

where $\mathbf{n}$ is the unit outward normal to the surface S , the double square bracket denotes a quantity jump across the surface from the inside to outside of the material, for example, $[[\bullet]] = [\bullet]^+ - [\bullet]^-$, where $[\bullet]^+$ and $[\bullet]^-$ are one-sided limits of the function $(\bullet)$ from the outward and inward normal directions, respectively.

After a pull-back to the reference configuration, the Eulerian Maxwell's equations (3.2) and (3.3) as well as relation (3.4) are presented respectively in the Lagrangian forms of [176]

$$\nabla_{\mathbf{x}} \times \mathbf{H} = 0 \quad (3.6)$$

$$\nabla_{\mathbf{x}} \cdot \mathbf{B} = 0 \quad (3.7)$$

$$\mathbf{B} = \mu_0 J \mathbf{C}^{-1} (\mathbf{H} + \mathbf{M}) \quad (3.8)$$

where $\nabla_{\mathbf{x}} \times (\bullet)$ and $\nabla_{\mathbf{x}} \cdot (\bullet)$ are the material curl and divergence operators with respect to $\mathbf{X}$, $\mathbf{C} = \mathbf{F}^T \mathbf{F}$ is the right Cauchy-Green tensor, and the Lagrangian counterparts of the magnetic variables are given by [183]

$$\mathbf{B} = J \mathbf{F}^{-1} \mathbf{b}, \quad \mathbf{H} = \mathbf{F}^T \mathbf{h}, \quad \mathbf{M} = \mathbf{F}^T \mathbf{m} \quad (3.9)$$

Similarly, the Lagrangian counterparts of jump conditions (3.5) are rewritten as

$$\mathbf{N} \cdot [[\mathbf{B}]] = 0, \quad \mathbf{N} \times [[\mathbf{H}]] = 0 \quad (3.10)$$

where $\mathbf{N}$ is the unit outward normal to the surface boundary S_0 .

3.3.3. Conservation of mass

By the law of mass conservation for transport of mass species, it is required that the time rate of the mass change within the control volume equals to the rate at which mass enters into the volume plus the rate at which mass is generated or lost within the control volume due to the source or sink, namely [207]

$$\frac{d}{dt} \left\{ \int_{V(t)} c_s dV \right\} = - \int_{S(t)} \mathbf{j}_s \cdot \mathbf{n} dS + \int_{V(t)} r_s dV \quad (3.11)$$

where c_s is the true concentration of solvent, $\mathbf{j}_s$ the true diffusion flux of solvent, r_s the number of solvents supplied across the material element per unit time, and $d(\bullet)/dt$ the material time derivative.

By the Reynolds transport and the divergence theorem [206], the local form of the mass conservation for solvent is written as

$$\dot{c}_s + c_s \nabla \cdot \mathbf{v}_s = -\nabla \cdot \mathbf{j}_s + r_s \quad (3.12)$$

where $\dot{c}_s$ refers to the material time derivative of c_s , and $\mathbf{v}_s$ the convection flow velocity.

For conversion of Equation (3.12) into an expression with nominal quantities, the nominal concentration C_s is associated with the true concentration c_s by $C_s = c_s \det(\mathbf{F})$, and the nominal flux $\mathbf{J}_s$ with the true flux $\mathbf{j}_s$ by Nanson's relation $\mathbf{J}_s = \mathbf{J}\mathbf{F}^{-1}\mathbf{j}_s$. [206]. As a result, the conservation of solvent is rewritten in the Lagrangian form of [207]

$$\dot{C}_s = -\nabla_{\mathbf{x}} \cdot \mathbf{J}_s + R_s \quad (3.13)$$

where R_s is the rate of mass supply per nominal material element and $R_s = r_s \det(\mathbf{F})$.

3.3.4. Conservation of momentum

By the conservation of momentum, the mechanical deformation of the hydrogel is given by

$$\frac{d}{dt} \left\{ \int_{V(t)} \rho_h \mathbf{V}_h dV \right\} = \int_{S(t)} \boldsymbol{\sigma} \cdot \mathbf{n} dS + \int_{V(t)} \rho_h \mathbf{f}_b dV \quad (3.14)$$

where ρ_h is the true mass density of the hydrogel, $\mathbf{V}_h$ the deformation velocity, $\boldsymbol{\sigma}$ the Cauchy stress, and $\mathbf{f}_b$ the body force per mass including magnetic and mechanical body forces. In a magnetoelastic system, the magnetic body force is defined as $\rho_h \mathbf{f}_m = \mu_0 \nabla \mathbf{h} \cdot \mathbf{m}$ [170].

By the Reynolds transport and the divergence theorem [206], the mechanical equilibrium equation (3.14) is pulled back to Lagrangian configuration in a local form of

$$\rho_0 \dot{\mathbf{V}}_h = \nabla_{\mathbf{x}} \cdot \mathbf{P} + \rho_0 \mathbf{f}_b \quad (3.15)$$

where ρ_0 is the nominal mass density of the polymer network and $\rho_0 = J\rho_h$, $\mathbf{P}$ the first Piola-Kirchhoff stress and $\mathbf{P} = J\boldsymbol{\sigma}\mathbf{F}^{-T}$.

3.3.5. Energies in the hydrogel system

The rate of total energy of the magnetic hydrogel $\dot{\mathcal{E}}$ is defined as the rate of the integral of total energy density e over the volume V , and is contributed by four energy components, the thermal power $\dot{Q}$, the mechanical power $\dot{W}$, the chemical power $\dot{C}$, and the magnetic power $\dot{M}$. As a result, we have

$$\dot{\mathcal{E}} = \frac{d}{dt} \left\{ \int_V e dV \right\} = \dot{Q} + \dot{W} + \dot{M} + \dot{C} \quad (3.16)$$

It is known that heating mainly contributes to the internal energy change. The heat supply results from the thermal flux $\mathbf{q}$ entering into the system and the heat generation r_q within the system, such that the thermal power $\dot{Q}$ is given by [208]

$$\dot{Q} = - \int_S \mathbf{q} \cdot \mathbf{n} dS + \int_V r_q dV \quad (3.17)$$

The mechanical power $\dot{W}$ is contributed by the traction force $\mathbf{t}$ and the body force $\mathbf{f}_b$ acting on the hydrogel, namely

$$\dot{W} = \int_S \mathbf{t} \cdot \mathbf{V}_h dS + \int_V \rho_h \mathbf{f}_b \cdot \mathbf{V}_h dV \quad (3.18)$$

The chemical power $\dot{C}$ may vary due to the diffusion of solvent molecules into and out of the volume V , or mass generation r_s by chemical reaction. Thereby, the power of chemical energy $\dot{C}$ is given by [2]

$$\dot{C} = -\int_S \mu_s \mathbf{j}_s \cdot \mathbf{n} dS + \int_V \mu_s r_s dV \quad (3.19)$$

where μ_s is the chemical potential of solvent.

The magnetic power $\dot{M}$ is associated with the magnetization of the magnetic hydrogel by [172, 209]

$$\dot{M} = -\int_V \mathbf{m} \cdot \dot{\mathbf{b}} dV \quad (3.20)$$

By summation of Equations (3.17) to (3.20), the divergence theorem, the mass conservation equation (3.12), and replacing the traction force $\mathbf{t}$ with $\boldsymbol{\sigma} \cdot \mathbf{n}$, the rate of total energy $\dot{\mathcal{E}}$ is determined by

$$\frac{d}{dt} \left\{ \int_V e dV \right\} = \int_V \{ r_q - \nabla \cdot \mathbf{q} + (\nabla \cdot \boldsymbol{\sigma} + \rho_h \mathbf{f}_b) \cdot \mathbf{V}_h + \boldsymbol{\sigma} : \nabla \mathbf{V}_h + \mu_s \dot{c}_s - \mathbf{j}_s \cdot \nabla \mu_s - \mathbf{m} \cdot \dot{\mathbf{b}} \} dV \quad (3.21)$$

If $\dot{E}$ denotes the rate of total energy per unit reference volume, the left-hand side of Equation (3.21) is rewritten as [209]

$$\frac{d}{dt} \left\{ \int_V e dV \right\} = \int_{V_0} \dot{E} dV_0 \quad (3.22)$$

Similarly, in terms of the right-hand side of Equation (3.21), we have

$$\int_V (r_q - \nabla \cdot \mathbf{q}) dV = \int_{V_0} (R_q - \nabla_{\mathbf{x}} \cdot \mathbf{Q}) dV_0 \quad (3.23)$$

$$\int_V \{(\nabla \cdot \boldsymbol{\sigma} + \rho_h \mathbf{f}_b) \cdot \mathbf{V}_h + \boldsymbol{\sigma} : \nabla \mathbf{V}_h\} dV = \int_{V_0} [(\nabla_{\mathbf{x}} \cdot \mathbf{P} + \rho_0 \mathbf{f}_b) \cdot \mathbf{V}_h + \mathbf{P} : \mathbf{F}] dV_0 \quad (3.24)$$

$$\int_V (\mu_s \dot{c}_s - \mathbf{j}_s \cdot \nabla \mu_s) dV = \int_{V_0} (\mu_s \dot{C}_s - \mathbf{J}_s \cdot \nabla_{\mathbf{x}} \mu_s) dV_0 \quad (3.25)$$

$$\int_V \mathbf{m} \cdot \dot{\mathbf{b}} dV = \int_{V_0} [-(\mathbf{M} \cdot \mathbf{B} \cdot \mathbf{F}^{-T}) : \dot{\mathbf{F}} + (\mathbf{F}^{-T} \cdot \mathbf{M} \otimes \mathbf{B}) : \dot{\mathbf{F}} + \mathbf{M} \cdot \dot{\mathbf{B}}] dV_0 \quad (3.26)$$

where $\mathbf{Q}$ denotes the nominal heat flux and $\mathbf{Q} = \mathbf{JF}^{-1} \mathbf{q}$, R_q the material heat generation and $R_q = Jr_q$. It is noted that Equation (3.26) is achieved by the relations (3.9)₁ and (3.9)₃ together with the kinetic relation $\dot{\mathbf{J}} = \mathbf{JF}^{-T} : \dot{\mathbf{F}}$. Therefore, the material counterpart of Equation (3.21) is further rewritten as

$$\begin{aligned} \int_{V_0} \dot{E} dV_0 = & \int_{V_0} [(R_q - \nabla_{\mathbf{x}} \cdot \mathbf{Q}) + (\nabla_{\mathbf{x}} \cdot \mathbf{P} + \rho_0 \mathbf{f}_b) \cdot \mathbf{V}_h \\ & + (\mathbf{P} + \mathbf{M} \cdot \mathbf{B} \cdot \mathbf{F}^{-T} - \mathbf{F}^{-T} \cdot \mathbf{M} \otimes \mathbf{B}) : \dot{\mathbf{F}} + \mu_s \dot{C}_s - \mathbf{J}_s \cdot \nabla_{\mathbf{x}} \mu_s - \mathbf{M} \cdot \dot{\mathbf{B}}] dV_0 \end{aligned} \quad (3.27)$$

In general, the rate of total energy $\dot{\mathcal{E}}$ is equal to the sum of the rate of kinetic energy $\dot{K}$ and the internal energy $\dot{U}$, namely

$$\int_{V_0} \dot{E} dV_0 = \dot{K} + \dot{U} = \int_{V_0} \rho_0 \mathbf{V}_h \cdot \dot{\mathbf{V}}_h dV_0 + \int_{V_0} \dot{u} dV_0 \quad (3.28)$$

where u denotes the internal energy per unit reference volume.

From Equation (3.28) and the mechanical equilibrium equation (3.15), the local form of Equation (3.27) is rewritten as

$$\dot{u} = R_q - \nabla_{\mathbf{x}} \cdot \mathbf{Q} + (\mathbf{P} + \mathbf{M} \cdot \mathbf{B} \cdot \mathbf{F}^{-T} - \mathbf{F}^{-T} \cdot \mathbf{M} \otimes \mathbf{B}) : \dot{\mathbf{F}} + \mu_s \dot{C}_s - \mathbf{J}_s \cdot \nabla_{\mathbf{x}} \mu_s - \mathbf{M} \cdot \dot{\mathbf{B}} \quad (3.29)$$

3.3.6. Second law of thermodynamics for constitutive equations

By the second law of thermodynamics, it is stated that the integral of entropy per unit volume η increases as rapidly as the sum of the volume and surface heating divided by the absolute temperature T , as presented by the Clausius-Duhem inequality below [172]

$$\int_{V_0} \dot{\eta} dV \geq \int_{V_0} \frac{R_q}{T} dV_0 + \int_{S_0} \left(-\frac{\mathbf{Q} \cdot \mathbf{N}}{T} \right) dS_0 \quad (3.30)$$

By the divergence theorem, and then substituting the energy equation (3.29) to the inequality (3.30) by eliminating the rate of heat generation R_q , the inequality is rewritten in the local form of

$$T\dot{\eta} \geq \dot{u} - (\mathbf{P} + \mathbf{M} \cdot \mathbf{B} \cdot \mathbf{F}^{-T} - \mathbf{F}^{-T} \cdot \mathbf{M} \otimes \mathbf{B}) : \dot{\mathbf{F}} + \mathbf{M} \cdot \dot{\mathbf{B}} - \mu_s \dot{C}_s + \mathbf{J}_s \cdot \nabla_{\mathbf{x}} \mu_s + \frac{\mathbf{Q}}{T} \cdot \nabla_{\mathbf{x}} T \quad (3.31)$$

According to the thermodynamics, the density of Helmholtz free energy F is associated with the density of internal energy u via $F = u - T\eta$. If the free energy density F is a function of state depending on four independent variables, the absolute temperature T , the magnetic induction $\mathbf{B}$, the solvent concentration C_s , and the deformation gradient $\mathbf{F}$, we have

$$\begin{aligned} & -\left(\frac{\partial F}{\partial T} + \eta\right)\dot{T} + (\mathbf{P} + \mathbf{M} \cdot \mathbf{B} \cdot \mathbf{F}^{-T} - \mathbf{F}^{-T} \cdot \mathbf{M} \otimes \mathbf{B} - \frac{\partial F}{\partial \mathbf{F}}) : \dot{\mathbf{F}} - \left(\frac{\partial F}{\partial \mathbf{B}} + \mathbf{M}\right) \cdot \dot{\mathbf{B}} \\ & + \left(\mu_s - \frac{\partial F}{\partial C_s}\right)\dot{C}_s - \mathbf{J}_s \cdot \nabla_{\mathbf{x}} \mu_s - \frac{\mathbf{Q}}{T} \cdot \nabla_{\mathbf{x}} T \geq 0 \end{aligned} \quad (3.32)$$

The inequality (3.32) is derived directly on the basis of the second law of thermodynamics (3.30), which characterizes the present system, consisting of the magnetic hydrogel, magnetic field, and solvent environment, at arbitrary state including nonequilibrium and equilibrium. Therefore, the coefficient in any bracket vanishes, due to the arbitrariness of the variables, i.e. the absolute temperature T , the magnetic induction $\mathbf{B}$, the solvent concentration C_s , and the deformation gradient $\mathbf{F}$. Theoretically it is supposed that there are four dissipative terms that contribute to the entropy production, given by Equations (3.31) and (3.32), due to the present four independent variables. In the present model however, both the deformation gradient $\mathbf{F}$ and magnetic induction $\mathbf{B}$ are neglected for the contributions to the entropy production, based on the two reasons: (i) the significant time-scale difference between the short-time mechanical equilibrium and the long-range solvent migration [2, 210, 211], and between the short-time magnetic domain orientation and the long-time particle rotation [43], as well as (ii) the reversible processes of elastic deformation and paramagnetic magnetization [212]. As a result, the dissipation is mainly contributed by the two dissipative terms associated with the two independent variables, the absolute temperature T and concentration C_s . According to the linear irreversible thermodynamics, the phenomenological equations are written as [213, 214]

$$\mathbf{J}_s = L_{ss} \left(-\frac{1}{T} \nabla_{\mathbf{x}} \mu_s \right) + L_{sq} \left(\nabla_{\mathbf{x}} \frac{1}{T} \right) \quad (3.33)$$

$$\mathbf{Q} = L_{qs} \left(-\frac{1}{T} \nabla_{\mathbf{x}} \mu_s \right) + L_{qq} \left(\nabla_{\mathbf{x}} \frac{1}{T} \right) \quad (3.34)$$

where L_{ss} , L_{sq} , L_{qs} , and L_{qq} are the Onsager coefficients, and $L_{sq} = L_{qs}$ due to the Onsager relation. To make the inequality (3.32) held, the conditions for the coefficients $L_{ss} \geq 0$ and $L_{qq} \geq 0$ as well as for the off-diagonal elements satisfying $L_{ss}L_{qq} \geq (L_{sq} + L_{qs})^2/4$ are required. Consequently, Equation (3.32) is always larger than or equal to zero. Therefore, we have the constitutive equations that consist of two groups, one is to characterize the solvent flux, given by Equation (3.33), and the other is for the thermodynamic force as given below.

$$\eta = -\frac{\partial F}{\partial T}, \quad \mathbf{P} = \frac{\partial F}{\partial \mathbf{F}} - \mathbf{M} \cdot \mathbf{B} \cdot \mathbf{F}^{-T} + \mathbf{F}^{-T} \cdot \mathbf{M} \otimes \mathbf{B}, \quad \mathbf{M} = -\frac{\partial F}{\partial \mathbf{B}}, \quad \mu_s = \frac{\partial F}{\partial C_s} \quad (3.35)$$

If the magnetization $\mathbf{M}$ is employed as the independent variable, a complementary version of F is required, represented by Φ , through the Legendre transformation $\Phi = F + \mathbf{M} \cdot \mathbf{B}$ [215]. As a result, the refined thermodynamic forces are summarized as

$$\eta = -\frac{\partial \Phi}{\partial T}, \quad \mathbf{P} = \frac{\partial \Phi}{\partial \mathbf{F}} - \mathbf{M} \cdot \mathbf{B} \cdot \mathbf{F}^{-T} + \mathbf{F}^{-T} \cdot \mathbf{M} \otimes \mathbf{B}, \quad \mathbf{B} = \frac{\partial \Phi}{\partial \mathbf{M}}, \quad \mu_s = \frac{\partial \Phi}{\partial C_s} \quad (3.36)$$

3.3.7. Free energy density

To predict the response of the magnetic hydrogel, an explicit free energy density is required, and thus proposed here to account for the contributions from elastic deformation of the polymer networks Φ_{ela} , mixing of the polymers and solvent Φ_{mix} , and the magnetization Φ_{mag} , namely

$$\Phi = \Phi_{ela} + \Phi_{mix} + \Phi_{mag} \quad (3.37)$$

3.3.7.1. Elasticity

On the basis of the Gauss statistical model for rubber elasticity [216], the elastic free energy density Φ_{ela} is given as

$$\Phi_{ela} = \frac{1}{2} N k_B T \{ \text{tr}(\mathbf{F}^T \mathbf{F}) - 3 - 2 \ln[\det(\mathbf{F})] \} \quad (3.38)$$

where N is the effective number of polymer chains per unit reference volume, $G = N k_B T$ the shear modulus of hydrogel, and k_B the Boltzmann constant.

3.3.7.2. Mixing with the magnetic effect

By the Flory-Huggins polymer solution theory [216], the energy of mixing is expressed as

$$F_{mix} = k_B T [n_s \ln(1 - \phi_n) + \chi_H n_s \phi_n] \quad (3.39)$$

where n_s is the number of solvent at reference configuration, in which the hydrogel is undeformed, χ_H the Flory-Huggins parameter to characterize the interaction between the solvent and polymer networks, and ϕ_n the volume fraction of the polymer.

If the volume of the hydrogel changes only due to solvent absorption/desorption, the condition of molecular incompressibility is expressed as [211]

$$1 + v_s C_s = \det(\mathbf{F}) \quad (3.40)$$

where v_s is the volume per solvent species. In general, Equation (3.40) works as a constraint for the system in the equilibrium state, where the total energy of the system

reaches a minimum. For minimizing the system energy subject to a constraint, the constraint can be enforced by either a Lagrange multiplier Π , or eliminating a variable, in which they produce the same results. The present technique, i.e. using a Lagrange multiplier, maintains the deformation gradient $\mathbf{F}$ and concentration C_s as independent variables, and it employs the Lagrange multiplier Π to prescribe the constraint [211, 217, 218]. Therefore, the term $\Pi[1 + \nu_s C_s - \det(\mathbf{F})]$ is added into the total energy density Φ of the system (3.62).

If ξ_p denotes the volume fraction of magnetic particles for the magnetic hydrogel at reference state, the volume fraction of the polymer ϕ_n becomes $\phi_n = (1 - \xi_p) / \det(\mathbf{F})$ in the equilibrium state after swelling. By Equations (3.39) and (3.40), the free energy density for mixing is formulated as

$$\Phi_{mix} = \frac{k_B T}{\nu_s} [\nu_s C_s \ln(\frac{\nu_s C_s + \xi_p}{\det(\mathbf{F})}) + \chi_H \nu_s C_s \frac{1 - \xi_p}{\det(\mathbf{F})}] \quad (3.41)$$

It is found that the mixing energy density Φ_{mix} constructs a multiple coupling domain with the magneto-chemo-mechanical coupled fields, since the mixing energy density Φ_{mix} is a function of the magnetic particle concentration ξ_p , the solvent concentration C_s , and the mechanical deformation gradient $\mathbf{F}$.

3.3.7.3. *Magnetization associated with finite deformation for a general magnetic hydrogel*

As well known, when a magnetic hydrogel is placed in an external magnetic field $\mathbf{H}_0$, the hydrogel is magnetized and a demagnetization field $\mathbf{H}_d$ is thus induced due to the magnetized poles on the material boundary, in analogy to the polarization field in the presence of electric fields. In the present MECm model, a homogeneous magnetic field within the hydrogel is assumed. Such a field may be generated by a relatively long solenoid [80]. Therefore, the internal magnetic field $\mathbf{H}_i$ is the sum of demagnetization field $\mathbf{H}_d$ and the externally imposed field $\mathbf{H}_0$ by

$$\mathbf{H}_i = \mathbf{H}_0 + \mathbf{H}_d \quad (3.42)$$

where the demagnetization field $\mathbf{H}_d$ is associated with magnetization $\mathbf{M}$ by

$$\mathbf{H}_d = -N_d \mathbf{M} \quad (3.43)$$

where N_d is the demagnetizing factor of the hydrogel that depends on its geometry. If the internal magnetic intensity $\mathbf{H}_i$ is much smaller than that at saturation state $\mathbf{H}_s$, the magnetization $\mathbf{M}$ is linear with the magnetic field $\mathbf{H}_i$, namely $\mathbf{M} = \chi \mathbf{H}$. By Equations (3.42) and (3.43), the magnetization $\mathbf{M}$ is rewritten as

$$\mathbf{M} = \frac{\chi \mathbf{H}_0}{1 + N_d \chi} \quad (3.44)$$

where χ is the magnetic susceptibility to characterize magnetizability of magnetic hydrogel.

The magnetic energy density Φ_{mag} is given by [219]

$$\Phi_{mag} = \mathbf{M} \cdot \mathbf{B} \quad (3.45)$$

Considering the magnetic boundary condition given by Equation (3.10), the normal component of magnetic induction $\mathbf{B}$ is continuous across the material boundary [176], and thus $\mathbf{B} = \mu_0 \mathbf{H}_0$ [80]. By Equation (3.44), the magnetization Φ_{mag} is further written as

$$\Phi_{mag} = \frac{\mu_0 \chi H_0^2}{1 + N_d \chi} \quad (3.46)$$

For specification of the magnetization, two variables, the demagnetizing factor N_d and magnetic susceptibility χ , are required, which are associated with deformation.

Usually demagnetizing factor has three components and they obey the law below [220]

$$N_x + N_y + N_z = 1 \quad (3.47)$$

For simple geometrical shapes, the demagnetizing factors of the hydrogels are constant. For example, $N_x = N_y = N_z = 1/3$ for a sphere or cube, $N_x = N_y = 0$ and $N_z = 1$ for a slab with infinite lateral (along x -, y -axis) dimensions. The exact demagnetizing factor is also achieved even for an ellipsoidal shape, since the

demagnetizing field is uniform within the hydrogel [187]. For other shapes, however, no generalized formula exists, due to the nonuniformity of the magnetic field within the hydrogel. An alternative way for the demagnetizing factor is based on the volume-average method or relevant tabulated data from experiments [220, 221].

The magnetic susceptibility in the magnetic hydrogel may be an analogy to the permittivity in the dielectric elastomer or gel. When the degree of cross-link is low, the elastomer or gel may behave like a liquid and then the permittivity is deformation independent. Such kind of material is also called ideal dielectric elastomer or gel [222-224]. However, when the cross-link degree is not low, the permittivity of a general dielectric elastomer or gel may be associated with the deformation, which may change the responsive characteristic from compression to tension states [222, 225]. Similarly, the magnetic susceptibility is constant in an ideal magnetic hydrogel [43], whereas it may be deformation-dependent in a general magnetic hydrogel, as demonstrated by the experimental work [80, 226]. In the MECm model, the magnetic susceptibility associated with the finite deformation is presented below.

If the magnetic particles are distributed homogeneously in a polymeric matrix and linearly magnetized, the magnetic susceptibility of the hydrogel χ is given by [152]

$$\chi = \chi_p \xi_p \frac{\langle \mathbf{h}_p \rangle}{H_i} \quad (3.48)$$

where χ_p is the magnetic susceptibility of the magnetic particle, $\mathbf{h}_p$ the magnetic field in the magnetic particle, $\langle \mathbf{h}_p \rangle$ the volume average magnetic field over the positions of every particle, H_i the magnitude of the internal magnetic field $\mathbf{H}_i$.

For a spherical magnetic particle, its external magnetic field is equal to the internal field of the magnetic hydrogel $\mathbf{H}_i$. Therefore, the magnetic field inside the particle $\mathbf{h}_p^0$ is written as

$$\mathbf{h}_p^0 = \mathbf{H}_i + \mathbf{H}_d' \quad (3.49)$$

where “0” represents the initial state without interaction, and $\mathbf{H}_d'$ is the demagnetization field of the particle associated with its magnetization $\mathbf{M}_p$ via

$$\mathbf{H}_d' = -N_p \mathbf{M}_p \quad (3.50)$$

where $N_p = 1/3$ for a spherical particle. $\mathbf{M}_p$ is associated with the magnetic field $\mathbf{h}_p^0$ by

$$\mathbf{M}_p = \chi_p \mathbf{h}_p^0 \quad (3.51)$$

By Equations (3.49) ~ (3.51), $\mathbf{h}_p^0$ is calculated by [151]

$$\mathbf{h}_p^0 = \frac{3}{3 + \chi_p} \mathbf{H}_i \quad (3.52)$$

At the initial state without interaction, the average magnetic field $\langle \mathbf{h}_p \rangle$ is equal to the magnitude of $\mathbf{h}_p^0$, namely $\langle \mathbf{h}_p \rangle = h_p^0$, hence the initial magnetic susceptibility of the hydrogel χ_{m0} in Equation (3.48), is given as

$$\chi_{m0} = \frac{3\chi_p \xi_p}{3 + \chi_p} \quad (3.53)$$

which is the approximate result of the classical Maxwell-Garnett formula [150]. It is known that the particles are magnetized and the particle-particle interaction may change the average field $\langle \mathbf{h}_p \rangle$, if a magnetic field is imposed. Following Zubarev's work [152], the average field $\langle \mathbf{h}_p \rangle$ is achieved via a regular method of reflection.

As shown in Figure 3.1, in the absence of the external magnetic field, the magnetic moments of the two particles oriented randomly, as illustrated by the dashed arrows. When the magnetic field is applied, the particles are magnetized and their moments align quickly along the field direction, due to the Néel or the Brownian mechanism, as illustrated by the solid arrows [44, 153]. Simultaneously, the particle-particle interaction occurs. The magnetic moment of the first particle generates an additional magnetic field in the second particle, which increases the magnetic moment in the second particle and vice versa. If the procedures recycle for k times, the magnetic field in a particle may be determined by [152]

$$\mathbf{h}_p = \mathbf{h}_p^0 + \mathbf{h}_p' = \mathbf{h}_p^0 + \mathbf{h}_p^0 \sum_{k=1}^{\infty} (\alpha V_p \frac{3\cos^2 \theta - 1}{r^3})^k \quad (3.54)$$

where $\mathbf{h}_p'$ is the auxiliary magnetic field induced by another particle, V_p the particle volume, $\mathbf{r}$ the distance between the two particles, θ the angle between the field $\mathbf{H}_0$ and the radius-vector $\mathbf{r}$, and $\alpha = 3\chi_p/[4\pi(3 + \chi_p)]$. The power series in Equation (3.54) converges [152]. For simplicity, only the first term of the series is employed in the present model [151].

Figure 3.1. Schematic of the interaction between two magnetic particles.

As the hydrogel deforms, the relative position is changed between the particles. The average magnetic field $\langle \mathbf{h}_p \rangle$ is obtained by integration of the magnetic field over the possible positions of the other particles, namely [152]

$$\langle \mathbf{h}_p \rangle = \langle \mathbf{h}_p^0 + \mathbf{h}_p' \rangle = h_p^0 + \frac{\xi_p}{V_p} \int h_p'(\mathbf{r}) g(\mathbf{r}) d\mathbf{r} \quad (3.55)$$

where $g(\mathbf{r})$ is the spatial pair distribution function for the probability of finding the second particle at the distance $\mathbf{r}$ from the first particle. The function $g(\mathbf{r})$ was also used to analyze the polarization field of a dielectric elastomer with satisfactory coincidence

achieved between the experimental and theoretical results [227]. The function $g(\mathbf{r})$ is given by

$$g = g_0 + \delta g \quad (3.56)$$

where g_0 is pair distribution function for the present undeformed hydrogel, as given by [228]

$$g_0 = \begin{cases} 0 & r < d \\ 1 + 8\xi_p \left(1 - \frac{3r}{4d} + \frac{r^3}{16d^3}\right) & d < r < 2d \\ 1 & r > 2d \end{cases} \quad (3.57)$$

where d is the particle diameter. δg is the change of the function g due to the hydrogel deformation, and is written as [227]

$$\delta g = -\nabla \cdot (g_0 \mathbf{u}) = -(g_0 \nabla \cdot \mathbf{u} + \mathbf{u} \cdot \nabla g_0) \quad (3.58)$$

where the displacement vector $\mathbf{u}$ between the particles may be approximately taken as the hydrogel deformation, if an affine deformation is considered. In other words, the macroscopic deformation of the hydrogel is affinely mapped to the displacement of each particle [148]. Furthermore, no relaxation process is also assumed [52], in order to make Equation (3.58) held.

By Equations (3.55) and (3.56), the average magnetic field $\langle \mathbf{h}_p \rangle$ is rewritten as

$$\langle \mathbf{h}_p \rangle = h_p^0 + \frac{\xi_p}{V_p} \int h_p'(\mathbf{r}) g_0(\mathbf{r}) d\mathbf{r} + \frac{\xi_p}{V_p} \int h_p'(\mathbf{r}) \delta g(\mathbf{r}) d\mathbf{r} \quad (3.59)$$

By Equations (3.54), and (3.57) to (3.59), the average field $\langle \mathbf{h}_p \rangle$ is further rewritten as

$$\langle \mathbf{h}_p \rangle = [1 + \frac{8}{15} \xi_p \pi \alpha (1 - 5\xi_p)(\lambda_x + \lambda_y - 2\lambda_z)] h_p^0 \quad (3.60)$$

where λ_x , λ_y , and λ_z denote stretches along coordinate directions respectively.

Usually $\chi_p \gg 1$ and $\chi_p / (3 + \chi_p) \cong 1$ [45], by Equations (3.48) and (3.60), the susceptibility of the magnetic hydrogel χ is thus rewritten as

$$\chi = 3\xi_p [1 + \frac{2}{5} \xi_p (1 - 5\xi_p)(\lambda_x + \lambda_y - 2\lambda_z)] \quad (3.61)$$

where the first term represents the magnetic susceptibility of the undeformed hydrogel [150], and the second term the change of susceptibility of hydrogel due to the deformation. Therefore, it is concluded that the magnetic energy density $\Phi_{mag} = \mathbf{M} \cdot \mathbf{B}$, given by Equation (3.45), presents the magnetic field coupled with the mechanical field, since the magnetic energy density Φ_{mag} is a function of the demagnetizing factor N_d and magnetic susceptibility χ , which are associated with mechanical deformation, due to the magnetization $\mathbf{M} = \chi \mathbf{H}_0 / (1 + N_d \chi)$, given by Equation (3.44).

As expressed by Equation (3.37), the total free energy density Φ of the system is contributed by the elasticity, mixing, and magnetization. By summarization of Equations (3.38), (3.41), and (3.46), and considering molecular incompressibility (3.40), Φ is written below in detail

$$\begin{aligned} \Phi = & \frac{1}{2} N k_B T \{ \text{tr}(\mathbf{F}^T \mathbf{F}) - 3 - 2 \ln[\det(\mathbf{F})] \} + \frac{\mu_0 \chi H_0^2}{1 + N \chi} \\ & + \frac{k_B T}{v_s} [v_s C_s \ln(\frac{v_s C_s + \xi_p}{\det(\mathbf{F})}) + \chi_H v_s C_s \frac{1 - \xi_p}{\det(\mathbf{F})}] + \Pi [1 + v_s C_s - \det(\mathbf{F})] \end{aligned} \quad (3.62)$$

where the Lagrange multiplier Π is also interpreted as the osmotic pressure [211, 217].

So far the development of the present MECm model has been completed theoretically. It includes the Maxwell's equations (3.6) and (3.7), the conservation of mass (3.13), and the conservation of momentum (3.15). On the basis of the second law of thermodynamics, the constitutive equation (3.36) is formulated. Furthermore, the present MECm model includes the free energy density presented via (3.62). To simulate and analyze the performance of the magnetic hydrogel in the equilibrium state, the corresponding model reduction and boundary conditions are required and will be discussed in the following sections.

3.4. Reduction of the MECm model in the equilibrium state

In this section, the MECm model is reduced in the equilibrium state for magnetic-sensitive hydrogel subject to uniform and nonuniform magnetic field respectively.

3.4.1. A uniform magnetic field

In a uniform magnetic field, no field-particle interaction exists and the particle-particle interaction dominates, due to the lack of a field gradient [155]. If no mechanical load is considered for the equilibrium state, the mechanical equilibrium equation (3.15) is reduced to

$$\nabla_{\mathbf{x}} \cdot \mathbf{P} = 0 \quad (3.63)$$

If no external constraint exists, the stress over the hydrogel-solvent interface vanishes, namely $\mathbf{P} = 0$. In addition, the chemical potential μ_s inside the hydrogel, given by Equation (3.36), is equal to the external chemical potential $\mu_s^* = 0$ [229]. In the following validation and material optimization design, the performance of the magnetic hydrogel is investigated under a uniform magnetic field along the z -axis.

3.4.2. A nonuniform magnetic field

If a magnetic hydrogel is subjected to a nonuniform magnetic field generated by an electromagnet, four stages of responding process may exist, as shown in Figure 3.2: (i) the dry state of the hydrogel before immersed in the solvent, as shown in Figure 3.2(a); (ii) the free swelling state of the hydrogel before imposing the nonuniform magnetic field, as shown in Figure 3.2(b); (iii) the short-time responsive state of the hydrogel, as shown in Figure 3.2(c); and (iv) the long-time responsive state of the hydrogel, as shown in Figure 3.2(d). It is noted that the solvent inside the hydrogel has no time to migrate at the short-time scale, such that the concentration of solvent within the hydrogel remains unchanged and the hydrogel behaves like an incompressible elastomer [224, 230]. However, the solvent may migrate into the hydrogel gradually over a long-time scale, which allows the hydrogel to change both the shape and volume. All these states may induce large deformation, whereas different responsive behaviors may be included.

Figure 3.2. Four stages of response processes for the magnetic hydrogel at (a) the dry state, (b) the free swelling state, (c) the short-time responsive state, and (d) the long-time responsive state.

3.4.2.1. Free swelling

The hydrogel swells isotropically if no constraint exists. When it reaches an equilibrium state, stress vanishes, namely $P_x = P_y = P_z = 0$, and the chemical potential μ_s is also equal to zero, due to the absence of chemical driving force.

On the basis of the constitutive relation (3.36) and the free energy density (3.62), the free swelling stretch is obtained by

$$P_{x,y,z} = Nk_B T (\lambda_0 - \lambda_0^{-1}) - \Pi \lambda_0^2 = 0 \quad (3.64)$$

where λ_0 is the stretch at free swelling state and $\lambda_x = \lambda_y = \lambda_z = \lambda_0$, and the osmotic pressure Π in the equilibrium state is determined by setting $\mu_s = 0$

3.4.2.2. Short-time scale

If a nonuniform field is imposed, two distinct interactions exist, particle-particle and the field-particle interactions. The former results from the particle magnetization, and the latter from the magnetic field gradient. Generally, the deformation induced by the field-

particle interaction is much larger than that by particle-particle interaction [155]. As such, the magnetostriction due to the particle-particle interaction is negligible in a nonuniform magnetic field. If the inertial term is ignorable, the mechanical equilibrium equation (3.15) is rewritten as

$$\nabla_{\mathbf{x}} \cdot \mathbf{P} + J\mu_0 \mathbf{F}^{-T} \cdot \nabla_{\mathbf{x}} \mathbf{h} \cdot \mathbf{m} = 0 \quad (3.65)$$

If the magnetic field along the z -axis direction is not perturbed by adding the magnetic hydrogel, the magnetic force is parallel to field line. Integrating Equation (3.65) gives

$$P_z + \frac{J}{\lambda_z} \int_{h_b}^{h_t} \mu_0 m_z dh_z = 0 \quad (3.66)$$

where m_z and h_z are the magnitudes of the magnetization and magnetic intensity, respectively, h_t and h_b the magnitudes of the magnetic intensity on the top and bottom surfaces of the hydrogel respectively.

At a short-time scale, the volume of the hydrogel is kept unchanged. By Equations (3.36) and (3.62), the stress due to elasticity is given by

$$P_z = Nk_B T \left(\lambda_z - \frac{1}{\lambda_z^2} \right) \quad (3.67)$$

where λ_z is the hydrogel stretch along the magnetic field direction.

Inserting Equation (3.67) into Equation (3.66), we have

$$Nk_B T(\lambda_z - \frac{1}{\lambda_z^2}) + \lambda_z^{-1} \int_{h_b}^{h_t} \mu_0 m_z \cdot dh_z = 0 \quad (3.68)$$

For solution of Equation (3.68), the classical Langevin function is employed to relate magnetic intensity $\mathbf{h}$ with magnetization $\mathbf{m}$ by [89]

$$\mathbf{m} = \xi_p \mathbf{m}_{sat} (\coth \varsigma - 1/\varsigma) \quad (3.69)$$

where $\mathbf{m}_{sat}$ is the saturation magnetization of the magnetic particle, ς the Langevin parameter and $\varsigma = \mu_0 m_p h_z / (k_B T)$, where m_p is the magnetic moment of the particle.

Substituting Equation (3.69) into (3.68), the stretch λ_z at short-time scale is thus obtained by

$$Nk_B T(\lambda_z - \frac{1}{\lambda_z^2}) + \xi_p m_{sat} \frac{k_B T}{\lambda_z m_p} (\ln \frac{\sinh \varsigma_t}{\varsigma_t} - \ln \frac{\sinh \varsigma_b}{\varsigma_b}) = 0 \quad (3.70)$$

3.4.2.3. Long-time scale

Over a long time, the hydrogel is able to absorb additional solvent due to the imbalance of the chemical potential μ_s between the interior hydrogel and exterior solvent, and its volume is thus changed. Based on the constitutive equation (3.36), the stresses in transverse and field directions are obtained respectively as

$$P_x = Nk_B T(\lambda_x - \lambda_x^{-1}) - \Pi \lambda_y \lambda_z \quad (3.71)$$

$$P_y = Nk_B T(\lambda_y - \lambda_y^{-1}) - \Pi \lambda_x \lambda_z \quad (3.72)$$

$$P_z = Nk_B T(\lambda_z - \lambda_z^{-1}) - \Pi \lambda_x \lambda_y \quad (3.73)$$

where the osmotic pressure Π in the equilibrium state is obtained by setting $\mu_s = 0$.

If no constraint exists, the equilibrium stress is zero in the transverse direction. In the magnetic field direction, the stress P_z is required to equilibrate with stress by the magnetic effect given by

$$P_z = -\xi_p m_{sat} \frac{J}{\lambda_z} \frac{k_B T}{m_p} \left(\ln \frac{\sinh \varsigma_t}{\varsigma_t} - \ln \frac{\sinh \varsigma_b}{\varsigma_b} \right) \quad (3.74)$$

Therefore, the hydrogel deformation is obtained by Equations (3.71) to (3.74).

3.5. Extension of the MECm model with consideration of moving fluid

For applications in diverse areas including microfluidics and drug delivery, the hydrogel is often immersed in a moving fluid instead of still fluid, where the hydrostatic pressure may impede the hydrogel swelling by overcoming the osmotic pressure and it may cause the hydrogel to collapse [231]. A literature search shows that so far no effort has been done to reveal the responsive mechanism of the magnetic hydrogel under the coupled magneto-chemo-hydro-mechanical fields. Therefore, it is worthwhile to extend the MECm model developed in Section 3.3 to include the effect of hydrodynamic field, for quantitative characterization of the transient fluid-structure interaction of the deformable magnetic hydrogel with surrounding fluid flow.

For the moving fluid, the incompressible Navier-Stokes equations [232] are employed to describe the fluid flow with the microchannel in microfluidic system, namely

$$\nabla \cdot \mathbf{v}_s = 0 \quad (3.75)$$

$$\rho_s \frac{\partial \mathbf{v}_s}{\partial t} + \rho_s (\mathbf{v}_s \cdot \nabla) \mathbf{v}_s = \nabla \cdot \boldsymbol{\sigma}_s + \rho_s \mathbf{g} \quad (3.76)$$

where $\nabla(\bullet)$ denotes the spatial gradient operator with respect to the Eulerian coordinate $\mathbf{x}$. ρ_s , $\mathbf{v}_s$ and $\mathbf{g}$ represent the fluid mass density, velocity, and gravitational acceleration respectively. The fluid stress tensor $\boldsymbol{\sigma}_s$ is expressed as $\boldsymbol{\sigma}_s = -p\mathbf{I} + \varphi[\nabla_{\mathbf{x}}\mathbf{v}_s + (\nabla_{\mathbf{x}}\mathbf{v}_s)^T]$ [232], where $\mathbf{I}$, p and φ represent the second rank identity tensor, the fluid pressure, and dynamic viscosity respectively.

Over the hydrogel-solvent interface S_0 , the kinetic and dynamic conditions are given below [232]

$$\mathbf{v}_s = \dot{\mathbf{u}}, \quad \mathbf{n} \cdot \boldsymbol{\sigma} = \mathbf{n} \cdot (\boldsymbol{\sigma}_s + \boldsymbol{\sigma}_m) \quad (3.77)$$

where $\mathbf{u}$ is the hydrogel displacement, $\boldsymbol{\sigma}_m = \mathbf{h} \otimes \mathbf{b} - (\mathbf{h} \cdot \mathbf{b})\mathbf{I}$ the Maxwell stress tensor in Eulerian form associated with its Lagrangian form $\mathbf{P}_m$ by $\boldsymbol{\sigma}_m = J^{-1}\mathbf{P}_m\mathbf{F}^T$.

It is known from Equation (3.35) that the magnetic induction vector $\mathbf{B}$ is employed as the independent variable. For simplification of the constitutive equations, the augmented free energy density Ψ is introduced by the Legendre transformation $\Psi = F + (\mathbf{C} : \mathbf{B} \otimes \mathbf{B})/(2\mu_0 J)$, such that the constitutive equation (3.36) is rewritten as

$$\eta = -\frac{\partial \Psi}{\partial T}, \quad \mathbf{P} = \frac{\partial \Psi}{\partial \mathbf{F}}, \quad \mathbf{H} = \frac{\partial \Psi}{\partial \mathbf{B}}, \quad \mu_s = \frac{\partial \Psi}{\partial C_s} \quad (3.78)$$

If the magnetic intensity $\mathbf{H}$ is employed as the independent variable, the augmented energy of Ω is required with partial Legendre transformation via $\Omega = \Psi - \mathbf{H} \cdot \mathbf{B}$ [209, 215], such that the constitutive equation (3.36) is rewritten as

$$\eta = -\frac{\partial \Omega}{\partial T}, \quad \mathbf{P} = \frac{\partial \Omega}{\partial \mathbf{F}}, \quad \mathbf{B} = -\frac{\partial \Omega}{\partial \mathbf{H}}, \quad \mu_s = \frac{\partial \Omega}{\partial C_s} \quad (3.79)$$

To accurately characterize the transient magnetic field distribution over the domains covering the magnetic hydrogel and its surrounding solvent, the magnetic intensity vector $\mathbf{H}$ is employed as the independent variable. If the linear magnetic behavior of the magnetic hydrogel is considered, the augmented free energy density Ω in reference configuration is given by [233]

$$\begin{aligned} \Omega = & \frac{1}{2} Nk_B T \{ \text{tr}(\mathbf{F}^T \mathbf{F}) - 3 - 2 \ln[\det(\mathbf{F})] \} - \frac{J\mu_m}{2} [(\mathbf{F}^{-T} \mathbf{H}) \cdot (\mathbf{F}^{-T} \mathbf{H})] \\ & + \frac{k_B T}{v_s} [v_s C_s \ln(\frac{v_s C_s + \xi_p}{\det(\mathbf{F})}) + \chi_H v_s C_s \frac{1 - \xi_p}{\det(\mathbf{F})}] + \Pi [1 + v_s C_s - \det(\mathbf{F})] \end{aligned} \quad (3.80)$$

where μ_m is the magnetic permeability and associated with the relative permeability μ_{mr} via $\mu_m = \mu_0 \mu_{mr}$.

From the free energy density (3.80) and the constitutive relation (3.79), the stress $\mathbf{P}$, the magnetic induction $\mathbf{B}$, and the chemical potential μ_s are expressed respectively as

$$\mathbf{P} = Nk_B T (\mathbf{F} - \mathbf{F}^{-T}) - \Pi \mathbf{F}^{-T} + J\mu_m \mathbf{F}^{-T} (\mathbf{H} \otimes \mathbf{H}) \mathbf{C}^{-1} - \frac{1}{2} J\mu_m \mathbf{F}^{-T} [(\mathbf{C}^{-1} \mathbf{H}) \cdot \mathbf{H}] \quad (3.81)$$

$$\mathbf{B} = J\mu_m \mathbf{C}^{-1} \mathbf{H} \quad (3.82)$$

$$\mu_s = k_B T \left[\ln \left(\frac{vC_s + \xi_p}{1 + vC_s} \right) + \frac{1 - \xi_p}{1 + vC_s} + \chi_H \left(\frac{1 - \xi_p}{1 + vC_s} \right)^2 \right] + \Pi v_s \quad (3.83)$$

From Equation (3.33), if an isothermal condition is assumed in the hydrogel system, the diffusion flux $\mathbf{J}_s$ is rewritten as [211]

$$\mathbf{J}_s = \frac{C_s D_s \mathbf{C}^{-1}}{k_B T} \nabla_{\mathbf{x}} \mu_s \quad (3.84)$$

where D_s denotes the diffusion coefficient.

Based on Equation (3.6), the magnetic intensity vector $\mathbf{H}$ relates to the magnetic scalar potential ψ by $\mathbf{H} = -\nabla_{\mathbf{x}} \psi$. By Equations (3.7) and (3.82), the magnetic potentials ψ in both the magnetic hydrogel and the exterior solvent satisfy

$$\nabla_{\mathbf{x}} \cdot (J \mu_m \mathbf{C}^{-1} \nabla_{\mathbf{x}} \psi) = 0 \quad (3.85)$$

To solve the governing equations with its corresponding constitutive relations, Dirichlet and/or Neumann boundary conditions are required and they are summarized as follows.

At the inlet of the fluid channel, we have

$$\psi = \psi(\mathbf{X}, t), \quad p = p_i \quad (3.86)$$

where p_i is the pressure of the fluid flow at the inlet, $\psi = \psi(\mathbf{X}, t)$ the prescribed magnetic potential constructed from the measured magnetic intensity.

At the outlet of the fluid channel, we have

$$\psi = \psi(\mathbf{X}, t), \quad p = 0 \quad (3.87)$$

At the walls of the fluid channel, the velocity $\mathbf{v}_s$ vanishes due to the non-slip condition, namely

$$\psi = \psi(\mathbf{X}, t), \quad \mathbf{v}_s = 0 \quad (3.88)$$

At the hydrogel-solution interface, we have the following boundary condition,

$$[[\psi]] = 0, \quad \mu_{mr} \frac{\partial \psi}{\partial N} \Big|_{\partial \beta^+} = \frac{\partial \psi}{\partial N} \Big|_{\partial \beta^-}, \quad \mu_s = \mu_s^*, \quad \mathbf{v}_s = \dot{\mathbf{u}}, \quad \mathbf{n} \cdot \boldsymbol{\sigma} = \mathbf{n} \cdot (\boldsymbol{\sigma}_s + \boldsymbol{\sigma}_m) \quad (3.89)$$

For the hydrogel system at initial time, the following conditions are used

$$\mu_s = \mu_{s0}, \quad \mathbf{v}_s = 0, \quad p = 0 \quad (3.90)$$

where the initial chemical potential of the hydrogel μ_{s0} is achieved via Equation (3.83) by setting stress $\mathbf{P} = 0$ in Equations (3.81) [210].

It is noted that the numerical problem may be caused at the early stage of swelling if the chemical potential on the hydrogel boundary μ_s is enforced to equal that of the surrounding solvent μ_s^* , when the external surface swells with a large swelling deformation, while the interior part of the hydrogel remains the dry state. The drastic discrepancy in deformation at different locations may result in relatively large compressive stress on the hydrogel boundary and may result in numerical problem in the

finite element simulation [234]. To address this issue, a smooth function over a short duration is imposed for the chemical potential at the hydrogel boundary.

So far the extended MECm model has been fulfilled theoretically for the magnetic hydrogel immersed in the solvent when subjected to the magnetic and hydrodynamic coupled fields. It consists of the magnetostatic equation (3.85), mechanical balance equation (3.15), the mass conservation equation (3.13), and the incompressible Navier-Stokes equations (3.75) and (3.76). In addition, the free energy density is presented via Equation (3.80), the constitutive relations given by Equations (3.81) ~ (3.84), as well as the corresponding boundary and initial conditions (3.86) ~ (3.90). The extended MECm model is numerically implemented by the finite element solver, COMSOL Multiphysics 5.3. It is known that the hydrogel deformation is conveniently formulated in a material frame by a Lagrangian description, whereas the fluid motion formulated in a spatial frame by an Eulerian description. To connect the interface between the material frame of the magnetic hydrogel and the spatial frame of the fluid, the fully coupled ALE algorithm is adopted for the fluid-structure interaction problem, which calculates the new mesh coordinates according to the movement of the hydrogel boundary [235]. Furthermore, the function of automatic remeshing is activated to ensure the calculation accuracy, when the mesh quality is below the critical value (e.g. 0.25).

3.6. Validations of the MECm model

In this section, the MECm model in the equilibrium state is validated by the comparisons of the theoretical results and the experiments for equilibrium swelling of magnetic hydrogel in responsive to a uniform magnetic field (Section 3.6.1), and nonuniform

magnetic field (Section 3.6.2). The extended MECm model is examined with (i) the finite element solution for transient hydrogel swelling (Section 3.6.3), (ii) the deformation of the magnetic hydrogel under a uniform magnetic field (Section 3.6.4), and (iii) the dynamic motion of a ferrofluid droplet (Section 3.6.5).

3.6.1. Equilibrium swelling of PAAm magnetic hydrogel subject to a uniform magnetic field

To examine the MECm model, a comparison is made with the experimental measurement by Safronov *et al.* [59] for the swelling of a square-shaped magnetic-sensitive hydrogel, in which polyacrylamide (PAAm) hydrogels with different volume fractions of magnetite particles were immersed in water for the deformation of the hydrogels with and without a uniform magnetic field, as shown in Figure 3.3. Initially, the magnetic hydrogel was in free swelling state without a magnetic field, and its dimensions were labeled L_{x0} , L_{y0} , L_{z0} , and $L_{x0} = L_{y0}$. After imposing the magnetic field along the z -axis, the hydrogel deforms with dimensions of L_x , L_y , L_z , and $L_x = L_y$. In the experiment [59], the deformation of the hydrogel is characterized by dimensional variation $\Delta_i = (L_i - L_{i0}) / L_{i0}$, where $i = x, y, \text{ or } z$, the volume change thus by $\Delta V = L_x L_y L_z / L_{x0} L_{y0} L_{z0} - 1$. Under the assumption of homogeneous deformation, the dimensional variation is rewritten as: $\Delta_i = \lambda_i - 1$. The demagnetizing factor for the hydrogel along the z -axis direction is approximated by $N_z = 1/(2n + 1)$ [221], where n is the dimensional ratio between axial and lateral directions, namely $n = L_z / L_x$. If f is the initial geometric factor, defined as

$f = L_{z0} / L_{x0}$, the factor N_z is rewritten as $N_z = \lambda_x / (2f\lambda_z + \lambda_x)$. The input parameters required for the MECm model are tabulated in Table 3.1.

Figure 3.3. Hydrogel swells at (a) the free swelling state, and (b) the current state with magnetic effect.

Table 3.1. Input parameters of the MECm model for the magnetic hydrogel subject to a uniform magnetic field.

parameters	symbol	value
Boltzmann constant	k_B	$1.38 \times 10^{-23} \text{ J/K}$
absolute temperature	T	298 K
volume per solvent molecule	v_s	10^{-28} m^3
volume fraction of magnetic particles	ξ_p	0~0.2 [59]
density of PAAm	ρ_{gel}	1350 kg/m^3 [25]
shear modulus of PAAm	G	0.43~55.3 kPa [236]
Flory-Huggins parameter	χ_H	0.12~0.23 [59]
vacuum magnetic permeability	μ_0	$4\pi \times 10^{-7} \text{ N/A}^2$
initial geometric factor	f	0.1~10

For a uniform magnetic field, the MECm model is examined in Figure 3.4 via comparison of the deformation of the magnetic hydrogel Δ_i along the field and

transverse directions, with different filled particle ratios $V_{particle}/V_{polymer}$, between the presented simulation results and the published experimental counterpart [59]. For plotting the figure, the deformation of the magnetic hydrogel Δ_i at the equilibrium state in a uniform magnetic field is determined by the constitutive equation (3.36), the free energy density (3.62), the governing equation (3.63), and the corresponding boundary condition $\mathbf{P} = 0$ and $\mu_s = 0$. The equations are solved numerically by the commercial finite element-solver, COMSOL Multiphysics 4.4. It is observed that the hydrogel elongates along the magnetic field direction and contracts in the transverse direction, when the ratio $V_{particle}/V_{polymer}$ is lower than 0.17. Such responsive behaviors were also observed by other experimental work [48, 49]. It is also seen from Figure 3.4 that, both the magnitudes of the elongation and contraction reach their maximum when the ratio $V_{particle}/V_{polymer}$ is around 0.1, then followed by a decreasing trend with the further increasing ratio $V_{particle}/V_{polymer}$. It is interesting that the hydrogel contracts along the field direction but elongates in the transverse direction, if the ratio $V_{particle}/V_{polymer}$ exceeds about 0.17. Probably the inversion results from the competition between the change of two factors, demagnetizing factor N_z and magnetic susceptibility χ [164]. The former induces the elongation of the hydrogel along the field direction, while the latter stimulates either elongation or contraction [151]. When the ratio $V_{particle}/V_{polymer}$ is low, the demagnetizing effect dominates and the hydrogel elongates with the field line. However, when the ratio $V_{particle}/V_{polymer}$ is high, the change of the magnetic susceptibility may play a more significant part in the contraction along the field direction [186].

Figure 3.4. Comparison of the present theoretical simulation and published experiment for the PAAM magnetic hydrogel subject to a uniform magnetic field [59].

3.6.2. Equilibrium deformation of PVA magnetic hydrogel subject to a nonuniform magnetic field

For a nonuniform magnetic field, the MECm model is validated and demonstrated in Figure 3.5, through a numerical comparison between the presently computational deformation of the magnetic hydrogel λ_z , numerically solved by Equation (3.70) via the COMSOL Multiphysics 4.4, and published experimental data [94] for a magnetic hydrogel immersed in solvent subject to a nonuniform magnetic field, as illustrated in Figure 3.2(b). As shown in Equation (3.69), the effect of nonlinear magnetization is included in the present model, such that it is applicable for either low or high magnetic field. In other words, the present model can be reduced for the low magnetic field with linear magnetization, similar to the work by *zriny et al.* [94] for the magnetoelastic equation formulated by linear magnetization. In addition, the effect of elasticity coupled with the magnetization induced by particle-particle interaction on the stress is also considered in the present model, given by Equation (3.15). In other words, the present

model can be reduced for the case with elasticity only, similar to the work by zriny *et al.* [94]. In summary, the present model can be reduced to the theory [94] if the particle-particle interaction and the nonlinear magnetization are ignored. The input data given in Table 3.2 includes the characteristic constant β for the field distribution, the current constant k_I obtained by fitting the experimental curves [94]. It is also found that the magnetic field maximizes near the magnet and decays exponentially away from the surface of the magnet, namely $h_z = h_{\max} e^{-\beta|z|}$, where the maximum magnetic field $h_{\max}$ is associated with the electric current I by $h_{\max} = k_I I$.

Table 3.2. Input parameters of the MECm model for the magnetic hydrogel subject to a nonuniform magnetic field.

parameter	symbol	value*
volume fraction of magnetic particles	ξ_p	0.024 [94]
magnetic distribution coefficient	β	0.4 [94]
saturation magnetization	m_{sat}	571 kA/m [237]
magnetic moment	m_p	$5.95 \times 10^{-20} \text{ Am}^2$ [94]
current constant	k_I	$7.32 \times 10^4 \text{ m}^{-1}$ [94]
shear modulus	G	1.2~2.5 kPa [94]
initial height	h_0	122.1 mm [94]

* All the parameters listed above are cited from the published experimental works in open literature for the present model validations

Figure 3.5. Comparison of the present theoretical simulation and published experiment for the PVA magnetic hydrogel subject to a nonuniform magnetic field [94], where the dots denote the experimental data, the solid and dashed lines the simulation results at stable and unstable states respectively.

Figure 3.5 illustrates the influence of initial magnet position z_0 on the deformation of the polyvinyl alcohol (PVA) magnetic hydrogel λ_z with the electrical current intensity I . The magnetic hydrogel is stretched significantly up to 165%, and exhibits the instability and hysteresis phenomena. Initially, the elongation λ_z increases slightly with increasing current I , and it exhibits maximum when $z_0 = 26.81$ mm, due to the decreasing magnetic field away from the magnet. When the current I increases up to a certain point, the increase of the elongation follows a step function with a significant change within a small range of the current I . As the current I increases further, the elongation increases linearly again and tends to the saturation gradually. Similarly, if the current I decreases, the hydrogel contracts and also exhibits the instability. However, the contraction does not follow the same path as the elongation, which is referred to as

hysteresis. The phenomena of instability and hysteresis in the magnetic hydrogel are also found in other soft materials, such as photo-sensitive hydrogel [238], temperature-sensitive hydrogel [239], magnetic drop [240], and ferrogel [43]. The present instability and hysteresis are analogous to the phase transition in material and may be characterized by the energy-stretch relation [96]. For example, if the initial magnet is positioned at $z_0 = 40.75$ mm with the small or large current ($I = 1$ A or 5A), the hydrogel energy W_T reaches a global minimum of the curve for total energy against hydrogel stretch, which corresponds to a stable phase, as shown in Figure 3.6(a). However, for the intermediate current ($I = 2.6 \sim 3.6$ A), a local maximum and two local minima occur, in which the local maximum represents an unstable phase, the lower minimum corresponds to a stable phase and the higher one to a metastable phase [239], as shown by the ABCD loop in Figure 3.6(b). It is found that Points E and F correspond to the current ($I = 3.2$ A) where the two minimum energies are equal each other. Since the energies along the paths AE and CF are smaller than those along the paths FD and EB, the stable equilibrium states are achieved along the paths AE and CF, and the metastable equilibrium states achieved along the paths FD and EB. The dashed path BD thus represents the unstable state. As the current I increases from 0 to around 3.8A, the hydrogel stretch λ_z increases from 1 to about 1.08 (at Point B), where the energy barrier between the two local minima vanishes and the metastable state of the hydrogel becomes unstable. The hydrogel stretch λ_z tends to the stable state (at Point C), such that an instability phenomenon occurs. If the current I increases continuously, the stretch λ_z increases further. However, when the current I decreases from 5.5A to about 2.6A, the hydrogel stretch λ_z decreases from 1.45 to about 1.35 (at Point D), where the energy barrier between the two local minima vanishes and

the metastable stable of the hydrogel becomes unstable again. As a result, the hydrogel stretch λ_z tends to the stable state (at Point A), and accordingly another instability phenomenon occurs. Therefore, the magnetic hydrogel undergoes the instability with a hysteresis loop when exposed to a nonuniform magnetic field.

Figure 3.6. Total energy of the magnetic hydrogel W_T as a function of stretch λ_z at several current intensities I when $z_0 = 40.75\text{mm}$, where the open and solid circles denote the local minima at small and large stretch respectively (a); Instability and hysteresis phenomena under a nonuniform magnetic field, where the arrows above the curve denote the direction of contraction and those below the curve denote the direction of extension (b).

3.6.3. Transient swelling of a constrained hydrogel slab

For examination of the extended MECm model, a comparison with the finite difference solution by Bouklas *et al.* [217] is made for 1D transient swelling of a hydrogel slab. The hydrogel is placed in a rigid container and its deformations are constrained in X_1 and X_3 directions, in which the top surface of the hydrogel is in contact with the solvent, while its bottom surface is fixed and no fluid is allowed to transport, as shown in Figure 3.7(a). In the validation, the model developed is reduced to a 2D computational domain and then compared with that achieved through a 1D finite difference method [217]. The boundary conditions are given below: the hydrogel displacement $\mathbf{u}|_{X_2=0}=0$, the solvent flux at the bottom surface $\mathbf{J}_s|_{X_2=0}=0$, the chemical potential at top surface $\mu_s|_{X_2=L_H}=0$, the hydrogel displacement along X_1 direction $u_1|_{X_1=-L_0, L_0}=0$ (Here $2L_0$ is the hydrogel length), and the solvent flux at lateral surfaces $\mathbf{J}_s|_{X_1=-L_0, L_0}=0$, respectively. The initial stretch along X_2 direction is set as $\lambda_0 = 1.4$, and the initial chemical potential $\mu_{s0}(\mathbf{X}, 0) = -0.035k_B T$ is determined by Equations (3.81) and (3.83). The input parameters include $L_H = 2L_0 = 1\text{ m}$, $D_s = 8 \times 10^{-9}\text{ m}^2/\text{s}$, $v_s = 10^{-28}\text{ m}^3$, $G = 40\text{ kPa}$, and $\chi_H = 0.4$ [217]. For simplification, the time t is normalized as the non-dimensional time $\bar{t} = tD_s / L_H^2$,

chemical potential μ_s as the non-dimensional chemical potential $\bar{\mu}_s = \mu_s / k_B T$, and the stress $\mathbf{P}$ as the non-dimensional stress $\bar{\mathbf{P}} = \mathbf{P} \mathbf{v}_s / k_B T$. Figure 3.7(b)-(d) are plotted to compare the present 2D numerical results with 1D finite difference solutions [217] for distributions of the non-dimensional chemical potential $\bar{\mu}_s$, the stretch λ_2 , and the non-dimensional compressive stress $\bar{P}_{X1}$, against the non-dimensional coordinate X_2 / L_H , at non-dimensional times $\bar{t} = 0.1, 10, 50, 200, 1000$, and t^* , respectively, where t^* represents a time for evolution of the swelling fully developed [217].

Figure 3.7. Schematic of the constrained hydrogel slab in transient swelling (a). Comparison of the present theoretical simulation (solid lines) with the finite difference solutions [217] (circles) for variation of the non-dimensional chemical potential $\bar{\mu}_s$ (b),

the stretch λ_2 (c), and the non-dimensional stress $\bar{P}_{x1}$ (d), against the non-dimensional coordinate X_2/L_H .

It is found from Figure 3.7 (b)-(d) that the chemical potential $\bar{\mu}_s$, the stretch λ_2 , and the compressive stress $\bar{P}_{x1}$ have the similar profile patterns, where the sharp gradients of $\bar{\mu}_s$, λ_2 , and $\bar{P}_{x1}$ are developed near the upper surface $X_2 = L_H$ at the early stage of swelling (e.g. $\bar{t} \leq 50$), then the gradients become smaller gradually (e.g. $\bar{t} \leq 1000$), and finally they vanish to reach the equilibrium state (e.g. $\bar{t} = \bar{t}^*$). Moreover, it is demonstrated that the increasing rate of the hydrogel stretch λ_2 decreases with non-dimensional time $\bar{t}$, as illustrated in Figure 3.7(c). It is because that the gradient of chemical potential $\bar{\mu}_s$ is large at the surface $X_2 = L_H$, and the compressive stress $\bar{P}_{x1}$ small in the interior part of the hydrogel during the initial swelling process, which both contribute to the solvent absorption and diffusion [234]. However, when more and more solvent enters into the hydrogel, the gradient of $\bar{\mu}_s$ becomes smaller and the compressive force $\bar{P}_{x1}$ larger, which both prevent the solvent penetrating into the hydrogel.

3.6.4. Equilibrium deformation of PDMS magnetic hydrogel subject to a uniform magnetic field

For further validation of the extended MECm model, the predicted equilibrium deformation of the magnetic hydrogel λ is compared with the experimental data [48], where the spherical magnetic polydimethylsiloxane (PDMS) hydrogel was synthesized and placed in a uniform magnetic field $\mathbf{H}_0$, as shown in Figure 3.8(a). The input parameters include: $L_R = 24 \text{ mm}$, $L_H = 40 \text{ mm}$, $R_0 = 3.225 \text{ mm}$, $G = 15 \text{ kPa}$,

$\mu_0 = 4\pi \times 10^{-7} \text{ N/A}$ and $\mu_{mr} = 1.12$. In the cylindrical coordinate with axial symmetry, only half of the computational domain is used. To achieve the distributive magnetic field, the far-field magnetic boundary condition is adopted [183], where the magnetic intensity remains uniform or unperturbed on the surrounding edge ∂S_0 . Therefore, Neumann type of the magnetic boundary condition is used at the symmetric axis and the lateral surrounding boundary, namely $\partial\psi/\partial R = 0$. Due to the relation $\mathbf{H} = \nabla_{\mathbf{x}}\psi$, the magnetic scalar potential $\psi = -H_0 Z + c$ is imposed at the upper and bottom surfaces of the surrounding, where c is a constant. As seen from Figure 3.8(b), the magnetic hydrogel elongates along the field direction and contracts in the transverse direction, and the deformation λ increases with the magnetic field H_0 . This is because magnetic force F_f is associated with the local magnetic field via $F_f = \mu_0(\mu_{mr} - 1)(H_t^2 + \mu_{mr}H_n^2)/2$ [241], where H_t and H_n are respectively the tangential and normal components of the magnetic fields over the hydrogel-surrounding interface. It is known that magnetic field is uniformly distributed inside the spherical hydrogel, and the tangential magnetic field $H_t = 0$ at the top and bottom apexes of the hydrogel. In addition, the relative magnetic permeability of the hydrogel μ_{mr} is higher than 1, such that the force F_f maximizes at the top and bottom apexes of hydrogel and thus makes the hydrogel deformed to the prolate spheroid [241].

Figure 3.8. Schematic of the magnetic hydrogel placed in surrounding air (a). Comparison of the present theoretical simulation (solid lines) and the experimental results [48] (square bricks) for the magnetic field-dependent deformation of the magnetic hydrogel in the equilibrium state (b).

3.6.5. Dynamic motion of a ferrofluid droplet

To examine the extended model for fluid-structure interaction of the ferrofluid droplet with the surrounding fluid, a comparison of theoretical simulation is made with the experimental data [242], where the spherical droplet was prepared by incorporation of the magnetite nanoparticles into carboxylate-functional PDMS, and its motion through a highly viscous medium was measured and recorded when subjected to a magnetic field gradient by a permanent magnet, as shown in Figure 3.9(a). In the validation, the magnetic boundary condition for the magnetic scalar potential due to the nonuniform magnetic field is constructed by the experimental measurement [242]. Without the magnetic droplet, the magnetic field was measured as a function of the distance Z from the surface of magnet, which is fitted by a fifth-degree polynomial,

$H(0, Z) = -2.62 \times 10^{10} Z^5 + 2.56 \times 10^9 Z^4 - 9.71 \times 10^7 Z^3 + 1.8 \times 10^6 Z^2 - 1.7 \times 10^4 Z + 69.26$ as shown in Figure 3.9(b). Based on the relation $\mathbf{H} = -\nabla_{\mathbf{x}} \psi$, the magnetic scalar

potential $\psi(0, Z)$ is given by a sixth-degree polynomial along the axial direction,

$$p_6(Z) = 4.37 \times 10^9 Z^6 - 5.12 \times 10^8 Z^5 + 2.43 \times 10^6 Z^4 - 6 \times 10^4 Z^3 + 8.5 \times 10^3 - 69.26Z + c \quad .$$

As the magnetic scalar potential ψ satisfies the Laplace's equation $\nabla_x^2 \psi = 0$ in the absence of magnetic droplet, the analytical solution of the magnetic potential ψ is obtained as $\psi(R, Z) = p_6(Z) - R^2 p_6^{(2)}(Z)/4 + R^4 p_6^{(4)}(Z)/64 - R^6 p_6^{(6)}(Z)/2304$ [243], which is then imposed on the fluid domain boundary ∂S_0 . The input parameters required by the present model include: $\rho_0 = 1320 \text{ kg/m}^3$ [242], $\varphi = 50 \text{ Pa} \cdot \text{s}$ [242], $\rho_s = 998 \text{ kg/m}^3$ [242], $G = 10 \text{ kPa}$ [244], $L_R = 4 \text{ mm}$, $L_H = 16 \text{ mm}$, and $\mu_{mr} = 2.4$.

Figure 3.9. (a) Schematic of a spherical magnetic droplet immersed in viscous fluid under a nonuniform magnetic field. (b) Fitting curve of the experimental measurement on magnetic field distribution along axial direction by a fifth-degree polynomial.

Table 3.3. Comparison of the travel times between the present numerical simulation and experimental, and theoretical results by Mefford *et al.*, [242] for droplets positioned at different initial distances with various diameters.

droplet diameter (mm)	initial droplet-magnet distance (mm)	simulation by Mefford <i>et al.</i> [242] (min)	simulation by present model (min)	experimental result (min)
1.0	12	21.2	13.2	15
1.8	12	6.6	5.3	4.0
2.0	11	3.2	2.8	2.5

Table 3.3 illustrates the comparisons of the numerical and experimental travel times for droplets with various diameters of 1, 1.8, and 2 mm and positioned at distances of 12, 12, and 11 mm respectively, where good agreements are achieved between the present simulation and experimental data [242]. As such, it is concluded that the multiphysics model can characterize well the response of the magnetic hydrogel. It is also observed that the relative error of theoretical result by Mefford *et al.* exceeds about 50%, probably the simulation regarded the droplet as a point dipole without consideration of the deformation coupled with its motion towards the magnet. However, the droplet size and the distance between the droplet and the magnet may have a significant effect on the transit time, which will be further discussed in the following sections by the validated model.

3.7. Remarks

A multi-effect-coupling magnetic-stimulus (MECm) model has been developed for numerical characterization of the magnetic hydrogel that is immersed in solvent subject to the external magnetic field. The present MECm model allows for finite deformation, and consists of the governing equations for the conservations of mass and momentum. In accordance with the second law of thermodynamics, several effects, such as the chemical potential, the magnetic field, and the finite deformation, are considered in the constitutive relations. In the MECm model, the magnetic susceptibility for magnetization of the general magnetic hydrogel is defined as a function of the finite deformation, instead of a constant for an ideal magnetic hydrogel. Moreover, a novel free energy density is proposed to consider the magnetic effects. After that, the MECm model is reduced in the equilibrium state, and then extended to consider the moving fluid, where the transient

fluid-structure interaction of the deformable hydrogel with the fluid flow is characterized through the fully coupled ALE algorithm. The MECm model is validated by comparisons with the finite difference solution and the published experimental data. Very good agreements are achieved between the comparisons, which are thus concluded that the presently developed model can well predict the behavior of the magnetic hydrogel with desired accuracy.

Chapter 4. Optimized Designs of Magnetic-Sensitive Hydrogel and Relevant Hydrogel-Based Devices

4.1. Introduction

Based on the MECm model developed in Chapter 3, this chapter optimizes the design of the magnetic-sensitive hydrogel and the relevant hydrogel-based devices, followed by the study of the influences of various material properties and magnetic parameters, in Section 4.2, on performance of the magnetic hydrogel in the equilibrium state, including hydrogel deformation and its instability and hysteresis under a uniform or nonuniform magnetic field. Subsequently, the transient performances of two magnetic hydrogel-based devices are investigated in Section 4.3 by the extended MECm model. The first is the magnetic-sensitive hydrogel-based microfluidic system for replicating various physiological and pathological conditions in the human body, by which the desired flow patterns can be generated in real time due to the fast-response deformation of the magnetic hydrogel. The second device is the magnetic-sensitive hydrogel-based drug targeting system for delivering the movable and deformable drug-loaded hydrogel to the specific site by variation of the inlet fluid flow velocity, the hydrogel size and position, the maximum magnetic field strength, and the magnet position. Finally, the remarks are presented in Section 4.4.

4.2. Optimized design of magnetic-sensitive hydrogel

In this section, comprehensive parameter studies are conducted based on the MECm model in Chapter 3, for optimization of design of magnetic-sensitive hydrogel immersed

in the solvent in the equilibrium state when subjected to externally applied magnetic field, including uniform and nonuniform magnetic fields.

4.2.1. A uniform magnetic field

To optimized design of the magnetic hydrogel immersed in solvent in response to a uniform magnetic field, several parameter studies with inputs given in Table 3.1 are carried out for effects of the shear modulus G , the magnetic induction B_z along direction of magnetic field, and the magnetic particle volume fraction ξ_p .

The first parameter study is performed to analyze the influence of shear modulus G on variation of dimensional change in the field and transverse directions as shown in Figure 4.1(a), and of volume change as shown in Figure 4.1(b), via Equations (3.36), (3.62) and (3.63), against the magnetic particle volume fraction ξ_p , where $f = 0.75$. As observed from Figure 4.1 (a), the shear modulus G influences the dimensional change Δ_i significantly when the volume fraction ξ_p ranges from 0.02 to 0.15. However, it has an insignificant effect on the dimensional change Δ_i when ξ_p is smaller than 0.02 or larger than 0.15. It is also seen from Figure 4.1(a) that the magnitude of Δ_i decreases in both the field and transverse directions with the increasing G . Probably the hydrogel deformation is contributed by the elastic, magnetic, and chemical effects. The larger shear modulus G strengthens the hydrogels and makes the polymer networks more compact. Since the osmotic pressure and the magnetic force as the driving sources are equilibrated by the elastic restoring force, the increase of G prevents the hydrogel from further stretching. Regarding the volume change ΔV , it deswells at first, then reaches the

minimum when ξ_p is around 0.11, as shown in Figure 4.1(b). After that, it recovers back to its free swelling state progressively and then swells continuously, when ξ_p increases further from 0.11 to 0.17.

Figure 4.1. (a) Influence of shear modulus G on the variation of dimensional change Δ_i with particle volume fraction ξ_p , (b) Influence of shear modulus G on the variation of volume change ΔV against particle volume fraction ξ_p .

Based on the constitutive equation (3.36), the governing equation (3.63), and the free energy density (3.62), Figure 4.2 is plotted for the variations of dimensional change Δ_i and volume change ΔV with magnetic induction B_z subject to different shear modulus G , where $f = 0.75$ and $\xi_p = 0.09$. As illustrated in Figure 4.2(a), the maximum dimensional change Δ_i is stimulated by the larger magnetic induction B_z and the smaller shear modulus G . It is also seen from Figure 4.2(b) that the swelling behavior of the magnetic hydrogel is much dependent on magnetic field applied, which was also demonstrated in the published experimental work [48, 99], where the volume swelling

ratio decreases when the magnetic induction B_z increases. We may understand this phenomenon by the well-known magnetization mechanism. Under externally imposed magnetic field, the interactions between the particles are enhanced, since magnetic moment of the magnetic particle tends to align along the field direction by the Néel and Brownian relaxations [43, 89]. As the particles are attached tightly onto the polymeric networks, the translations of magnetic particles stimulate the deswelling of the hydrogel.

Figure 4.2. (a) Influence of shear modulus G on the variation of dimensional change Δl with magnetic induction B_z , (b) Influence of shear modulus G on the variation of volume change ΔV against magnetic induction B_z .

4.2.2. A nonuniform magnetic Field

To optimized design of the magnetic hydrogel immersed in solvent subject to a nonuniform magnetic field at a long-time scale, as shown in Figure 3.2(d), numerous parameter studies are carried out to explore the effects of the initial magnet position z_0 , the current density I , and the volume fraction of magnetic particles ξ_p . For numerical simulation, the inputs of the parameters are given as follows. $\chi_H = 0.5$, $G = 1.4\text{ kPa}$,

$$v_s = 10^{-28} \text{ m}^2, \quad T = 298 \text{ K}, \quad \xi_p = 0.024, \quad \beta = 0.4, \quad m_{sat} = 571 \text{ kA/m},$$

$$m_p = 5.95 \times 10^{-20} \text{ A} \cdot \text{m}^2, \quad k_I = 7.32 \times 10^4 \text{ m}^{-1}, \text{ and } h_0 = 122.1 \text{ mm}.$$

By Equations (3.71) to (3.74), Figure 4.3 numerically illustrates the influence of the initial magnet position z_0 on the stretch λ_z along the field direction with the electric current I at short- and long-time scales, respectively. As seen from Figure 4.3, the instability and hysteresis phenomena are observed at both scales. However, the instability at the long-time scale starts at a lower current I and the width of hysteresis is much smaller than that at short-time scale. It is also found that the stretch λ_z is larger at long-time scale than that at short-time scale, resulted from the diffusion of the solvent.

Figure 4.3. Influence of initial magnet position z_0 on the variation of stretch λ_z along the field direction with current I under a nonuniform magnetic field.

The influence of the initial magnet position z_0 is illustrated numerically in Figure 4.4 on the swelling ratio of the magnetic hydrogel, through Equations (3.71) to (3.74),

against the electric current I at long-time scale. In the absence of the current I , the hydrogels are at the free swelling state and thus have the same swelling ratio. When the current I is applied, the swelling ratio also exhibits the instability and hysteresis, whereas the hysteresis width becomes smaller when the magnet position z_0 decreases from 50 to 30 mm, and even vanishes if $z_0 = 20$ mm. It is also noted that the swelling ratio tends to a saturation state when I is high. Probably the magnetization of the magnetic hydrogel, characterized by the Langevin equation, becomes saturated at the high magnetic field.

Figure 4.4. Influence of initial magnet position z_0 on the variation of swelling ratio with current I under a nonuniform magnetic field.

Based on Equations (3.71) to (3.74), Figure 4.5 demonstrates the influence of the volume fraction of magnetic particles ξ_p on the swelling ratio with the electric current I . As observed from the figure, in the absence of current I , the swelling ratio increases with the decrease of the particle volume fraction ξ_p , which is consistent with the

experimental measurement [99, 245]. Theoretically, the incorporation of the magnetic particles decreases the volume fraction of hydrophilic polymer networks, and thus reduces the ability of the hydrogel to imbibe solvent.

Figure 4.5. Influence of magnetic particle volume fraction ξ_p on the variation of swelling ratio with current I under a nonuniform magnetic field.

4.3. Optimized design of magnetic-sensitive hydrogel-based devices

With consideration of the transient fluid-structure interactions between the deformable hydrogel and the moving fluid, two magnetic-sensitive hydrogel-based devices are designed and optimized by the extended MECm model in Chapter 3, such as the microfluidic flow controller and the drug targeting system.

4.3.1. Microfluidic flow controller

4.3.1.1. Fast response behavior

As well known, the stimuli-sensitive hydrogel is widely used for self-regulated flow control in microfluidic chips [18], where its performance is generally associated with the

response rate of the hydrogel. As discussed previously, fast responsiveness is a remarkable feature of the magnetic hydrogel [143], whereas no effort was made to quantitatively characterize the behavior. To the best of our knowledge, it is the first theoretical study to reveal the property of the magnetic hydrogel. Here a transient simulation is performed for magnetic hydrogel immersed in surrounding solvent, when subjected to externally applied magnetic field. As demonstrated in Figure 4.6(a), the cylindrical magnetic hydrogel with outer radius R_o is placed in the microchannel of the microfluidic system, where the displacements of the top and bottom surfaces of the hydrogel are constrained by the channel wall, and the inner part of the magnetic hydrogel is coated on a fixed rod with the radius $R_i = 0.4R_o$. Thereby, it is reasonable to assume that the hydrogel deforms only in the radial direction, and a 2D transient simulation is thus conducted here to study the time-dependent responsive behavior of the hydrogel. The fluid is delivered to the microchannel with a constant inlet pressure p_i . Initially the hydrogel is at its dry state, and it then swells gradually to regulate the fluid flow. To improve the hydrogel response rate, a uniform magnetic field is imposed in the surrounding air.

Figure 4.6. Schematic of the magnetic hydrogel as microfluidic flow controller (a). Effect of the magnetic field H_0 on variation of fluid flow rate w against the time t when subjected to different hydrogel radii: $R_o = 200 \mu\text{m}$ (b), and $R_o = 250 \mu\text{m}$ (c), where the contours represent the hydrogel displacement under the field H_0 of 150 kA/m.

Figure 4.6(b) and (c) illustrate the effect of the external magnetic field H_0 on variation of average fluid flow rate w at the outlet of microchannel against the time t , where $R_o = 200 \mu\text{m}$ and $R_o = 250 \mu\text{m}$ respectively. The inputs of the parameters required for the numerical simulation include: $L_X = 6 \text{ mm}$, $L_Y = 4 \text{ mm}$, $L_C = 0.8 \text{ mm}$, $D_s = 8 \times 10^{-9} \text{ m}^2/\text{s}$, $\chi_H = 0.6$, $\varphi = 0.001 \text{ Pa s}$, $\rho_s = 1000 \text{ kg/m}^3$, $G = 100 \text{ kPa}$, and $\mu_{mr} = 3$. It is observed from the figures that, the flow rate w decreases with increasing

time t , where the rate w further decreases with the increase of the magnetic field H_0 . As shown in Figure 4.6(b), the flow rate w decreases drastically from about 4.5 to 1.1 ml/min, when subjected to the magnetic field H_0 of 150 kA/m, if the time t is less than 50 s. Subsequently, the rate w decreases slowly with a minimal variation from 1.1 to 0.4 ml/min during the following 150 s. After that, it approximates the steady state with $w=0.25$ ml/min. It is also found from Figure 4.6(b) that, the rate w at steady state is nonzero if magnetic field H_0 is 0 or 150 kA/m, while it becomes zero if $H_0 = 300$ kA/m, where the magnetic hydrogel contacts the microchannel wall and fully blocks the fluid stream. Therefore, the application of the external magnetic field accelerates the hydrogel swelling. Furthermore, it is seen that the flow rate w changes inversely with evolution of hydrogel swelling, where the hydrogel swells sharply at early stage, and then slowly until reaching an equilibrium state, as shown in the contours for hydrogel deformation under the magnetic field H_0 of 150 kA/m. As such, the flow manipulation may be realized by controlling the hydrogel deformation under the external magnetic field. As also demonstrated from Figure 4.6 (c), it is clearly known that the times required are different for the magnetic hydrogels to reach the closed state. For example, it takes about 15 s for the hydrogel under H_0 of 300 kA/m, while about 45 s and 70 s under H_0 of 150 kA/m and 0 respectively. Thereby, the response times for the magnetic hydrogels are improved by 78% and 35% respectively, when subjected to the magnetic fields H_0 of 300 and 150 kA/m, compared with free swelling hydrogel without magnetic effect. Therefore, the magnetic hydrogel with fast responsiveness may be potential as the flow controller in microfluidic chips and will be discussed in the following section.

4.3.1.2. *Flow pattern generation for various physiological/pathological conditions*

For accurate representation of human physiology, it is essential to simulate physiological and pathological conditions in microfluidic chips. In the present work, various patterns of pulsatile flows are generated to mimic the real cell physiological microenvironment experienced by the bone marrow stromal cells, and the pathological conditions at femoral artery during diastole and systole.

Figure 4.7 shows the reversible variation of the flow rate w with the time t at different inlet pressures p_i of 0.5 and 1 kPa, subject to magnetic field frequencies f_H of 0.015, 0.044, and 0.074 Hz respectively, where $R_o = 200 \mu\text{m}$ and $H_o = 200 \text{ kA/m}$. It is seen that the flow patterns generated are consistent with the real mechanical microenvironment experienced by the bone marrow stromal cells [246], indicating that the magnetic-sensitive hydrogel-based microfluidic system can be precisely controlled for formation of the physiological condition on demand within bone tissue. Apart from that, it is observed that the amplitude of the flow rate w can be altered by the inlet pressure p_i , and the frequency tuned by the external magnetic field frequency f_H . Moreover, no hysteresis in the frequency is found between the applied magnetic field and the resulting flow rate w , probably owing to fast-response deformation and excellent controllability of the hydrogel.

Figure 4.7. Flow pattern analysis under various conditions. The pulsatile flow patterns at the frequencies f_H of (a) 0.015 Hz, (b) 0.044 Hz, and (c) 0.074 Hz with the inlet pressure p_i of 0.5 kPa . The pulsatile flow patterns at the frequencies f_H of (d) 0.015 Hz, (e) 0.044 Hz, and (f) 0.074 Hz with the inlet pressure p_i of 1 kPa .

According to the Doppler ultrasound measurement, the femoral blood flow patterns may be categorized as the triphasic, biphasic, sharp monophasic, as well as poor monophasic waveforms, based on different levels of the peripheral arterial disease progression [247]. It is reported that the poor monophasic waveform is highly associated with atherosclerosis, and the sharp monophasic waveform associated with the stenosis at femoral arteries [247-249]. Therefore, it is crucial to implement such flow patterns in the microphysiological system to study the pathophysiology at the femoral artery, for deeper understanding of the fundamental mechanism underlying real events that occur in human body. However, it is challenging to create complex flow patterns by the conventional microfluidic chips [110]. A major advantage of the presently developed magnetic-sensitive hydrogel-based microfluidic system over the conventional microfluidic chips is its ability to generate the user-defined flow patterns. For example, when the externally applied magnetic field H_0 is prescribed to follow the pulsatile profile, as shown in Figure 4.8(a), the poor monophasic waveform is achieved with a blunted systole rise and a slow diastolic fall, as illustrated in Figure 4.8(b). When the magnetic field H_0 is prescribed to follow the profile, as demonstrated in Figure 4.9(a), the sharp monophasic flow is achieved with a sharp systole rise, and a slow diastolic fall, as well as a pause phase, as shown in Figure 4.9(b). Furthermore, it is noted that the waveforms simulated are consistent qualitatively with the real blood flow pattern in pathological condition [247], indicating the strong capability of the novel magnetic-sensitive hydrogel-based microfluidic device in manipulating the microfluidic flows for various microphysiological systems.

Figure 4.8. (a) Prescribed external magnetic field H_0 as a function of time t . (b) Generation of the pathological flow pattern for replication of the typical poor monophasic blood waveform at the common femoral artery.

Figure 4.9. (a) Prescribed external magnetic field H_0 as a function of time t . (b) Generation of the pathophysiological flow pattern for replication of the typical sharp monophasic blood waveform at the common femoral artery.

4.3.2. Drug targeting system

4.3.2.1. Performance of the magnetic hydrogel subject to various hydrogel size and location, and flow velocity

To provide an insight into the effects of hydrogel and suspending fluid on the targeting performance in the blood vessel, it is worthwhile to characterize the distributive magnetic field, the hydrogel deformation, and the transit time for the hydrogel to the targeting area. Herein, the motion and deformation of the magnetic hydrogel are investigated with the coupled effects of magneto-chemo-hydro-mechanical fields. To the best of our knowledge, it is the first attempt to study the fluid-structure interaction of the movable and deformable hydrogel with the moving fluid under a nonuniform magnetic field.

As illustrated in Figure 4.10(a), a 2D model is employed for the numerical simulation, since the variation along the direction perpendicular to the X - Y plane is assumed to be rather small during the transport of magnetic hydrogel [250]. The magnetic hydrogel is submerged in the biological fluid that is delivered to the blood vessel with a parabolic flow profile. The permanent magnet is located vertically at the coordinate $(L_X, 0.5L_Y)$, where the magnitude of field H maximizes at the surface of the magnet, and decays exponentially away along the X -axis direction, namely $H = H_{\max} e^{-0.2(X-L_X)}$. Initially the hydrogel is at its dry state, it then swells gradually and at the same time moves to the desired site, due to the magnetic and hydrodynamic effects. The inputs of the parameters required for the numerical simulation include: $L_X = 20 \text{ mm}$, $L_Y = 3 \text{ mm}$, $D_s = 2 \times 10^{-7} \text{ m}^2/\text{s}$, $\chi_H = 0.4$, $\rho_s = 1000 \text{ kg/m}^3$, $\varphi = 0.001 \text{ Pa} \cdot \text{s}$, $\mu_{mr} = 1.06$, $H_{\max} = 20 \text{ kA/m}$, $k_B T = 4.11 \times 10^{-21} \text{ J}$, and $G = 100 \text{ kPa}$.

Figure 4.10. Schematic of the magnetic-sensitive hydrogel placed in a moving fluid subject to a nonuniform magnetic field by a permanent magnet (a). Influence of the hydrogel radius R_0 on motion and deformation of the magnetic hydrogel (b), time evolution of the hydrogel displacement u (c), and time evolution of the swelling ratio (d).

Figure 4.10(b) is plotted to illustrate time evolution of the motion and deformation of the three hydrogels with varying radii, 0.1 mm, 0.15 mm, and 0.2 mm, respectively, where the maximum inlet flow velocity $v_{\max} = 0.1 \text{ mm/s}$. The magnetic hydrogel moves fast with increasing radius, which is qualitatively consistent with the relevant experimental findings [251] and theoretical results [250, 252] for magnetic particle-based drug delivery systems. It is because that the magnetic force is highly associated with the hydrogel radius [252, 253], where a larger hydrogel size results in stronger magnetic force acting on the hydrogel and thus the shorter time to reach the site of interest. It is also found from the figure that, no significant change is found in the movement of the three hydrogels when the time t is less than 10 s, while their movements vary drastically if t is larger than 20 s.

The hydrogel motion is shown more evidently in Figure 4.10(c), which demonstrates influence of the hydrogel radius R_0 on variation of the displacement u of the hydrogel center point with time. It reveals that: (i) initially the displacement u increases linearly until it reaches 7 mm; (ii) it then increases nonlinearly and sharply. This is because the magnetic field decays exponentially away from the permanent magnet, where it exhibits the highest field strength at the surface of the magnet. At the initial time step, the magnetic hydrogel is far away from the magnet, such that the magnetic effect is rather weak and the hydrogel movement is mainly determined by the fluid drag. When the hydrogel moves further to approach the magnet, the impact of the magnetic field increases gradually and then the hydrogel is accelerated towards the magnet. It is further found from Figure 4.10(b) that, the hydrogel swells during its motion, due to the diffusion of the fluid. In order to elucidate the swelling phenomenon, the time evolutions

of the average volume swelling ratios are demonstrated in Figure 4.10(d), where the three curves have the similar profile patterns. The hydrogels swell sharply at the early stage of swelling, and then its rate decreases smoothly. Theoretically, the hydrogel swelling is highly associated with the chemical driving force, i.e. the gradient of the chemical potential, which decreases with more and more fluid entering into the hydrogel [234]. It is noted that the transient swelling profile is consistent with experiment result by Zhuang *et al.* [254], which further verifies the capability of the developed model in predicting the hydrogel response. It is also found from the figure that the response rate of swelling is inversely proportional to the hydrogel radius, where the hydrogel with the smaller radius swells faster than that with the larger one. For example, the average swelling ratio increases from about 5.1 to 5.9 or 5.9 to 6.8 when the radius R_0 decreases from 0.2 to 0.15 or 0.15 to 0.1 mm respectively, when $t = 10$ s. Because the smaller hydrogel radius corresponds to a larger surface-to-volume ratio. When hydrogels are immersed in fluid, the hydrogel with smaller radius (i.e. higher surface-to-volume ratio) exhibits a faster stimuli response, due to the higher surface-to-volume ratio (i.e. smaller radius) leads to more contact with the surrounding solvent, as experimentally reported by Czugala *et al.* [255]. Furthermore, Figure 4.10(d) also illustrates the contours for distribution of swelling ratio of the hydrogel with $R_0 = 0.1$ mm. The ratio is distributed homogeneously at the dry state when $t = 0$. Immediately upon beginning of the swelling (e.g. $t = 2$ s), the hydrogel consists of regions with different degree of swelling, namely the outside surface swells much faster than that at the center of the hydrogel. As the swelling process approximates the equilibrium stage (i.e. $t = 32$ s), the swelling of the hydrogel tends to be homogeneous again. The interesting transient phenomenon observed during the hydrogel

swelling probably results from the relatively long diffusion time from the outside boundary to the inner core [234].

It is commonly known that the fluid flow velocity has a pronounced impact on the motion and deformation of the magnetic hydrogel, because there is a direct relationship between the shear stress and velocity field. To clarify this effect, the range of the maximum inlet flow velocity $v_{\max}$ is taken within 0.05~0.5 mm/s. The motion and deformation of the hydrogel are studied with the three maximum inlet velocities $v_{\max}$, 0.05 mm/s, 0.1 mm/s, and 0.5 mm/s, as shown in Figure 4.11(a). With increasing maximum initial velocity $v_{\max}$, the time decreases significantly from 31.1s to 25.1 s and to 11.9 s for the hydrogel moving from the initial position to the outlet. Because the shear stress is highly associated with the flow velocity, the hydrogel undergoes larger driving force from the hydrodynamic effect with increasing velocity $v_{\max}$. Therefore, the hydrodynamic effect is also required to be considered in the design and optimization of the magnetic drug targeting system. Figure 4.11(b) demonstrates the impact of the maximum inlet velocity $v_{\max}$ on the trajectory of the hydrogel center point with time. The movement speed increases with increasing velocity $v_{\max}$. When the displacement u reaches about 7 mm, the three hydrogels are suddenly accelerated towards the magnet, where the large magnetic field gradient occurs. To describe the transient swelling of the hydrogels during the hydrogel motion, Figure 4.11(c) is plotted for the time evolution of the average swelling ratio subject to different initial velocities $v_{\max}$. It is interesting that no noticeable change is found for the swelling process, probably due to the significant

time-scale difference between the short-time mechanical deformation by the hydrodynamic and magnetic fields and the long-time solvent migration [2, 131].

Figure 4.11. Influence of the maximum initial velocity $v_{\max}$ on (a) motion and deformation of the magnetic hydrogel, (b) time evolution of the hydrogel displacement u , and (c) time evolution of the swelling ratio.

Figure 4.12 is plotted for time evolution of the motion and deformation of the magnetic hydrogels located at three initial coordinates, (1 mm, -0.625 mm), (1 mm, 0), and (1 mm, 0.625 mm), respectively, where $v_{\max} = 0.1$ mm/s and $R_0 = 0.2$ mm. It is seen that the time t of 25.1 s is required for the hydrogel located at the centerline to reach the

end, while 25.7 s required for those at other positions. Because the profile of inlet flow velocity is parabolic, the shear stress is inverse to the distance from the hydrogel to the centerline of the vessel. It is interesting that all the three hydrogels may eventually be immobilized at the center of the outlet, due to the strong attracting force by the high magnetic field gradient close to the magnet surface.

Figure 4.12. Influence of the initial hydrogel position on motion and deformation of the magnetic hydrogel with time.

In general, the distribution of the magnetic field has a considerable influence on the behavior of motion and deformation of the magnetic hydrogel. Herein the spatial distribution of the non-dimensional magnetic intensity $H/H_{\max}$ at different times, 20, 25, and 25.1 s, along the horizontal line $Y=0$ is visualized in Figure 4.13(a) to (c) respectively, where the dash and solid lines denote the original magnetic field strength and the magnetic intensity in the presence of magnetic hydrogel respectively. The non-dimensional magnetic intensity $H/H_{\max}$ increases with increasing non-dimensional coordinate X/L_x , it then increases to a maximum at the hydrogel-fluid interface, where the intensity $H/H_{\max}$ follows a step function with a sharp decrease at the interface within a small range of the normalized coordinate X/L_x . Subsequently, it rises up to

another maximum until it reaches the interface again, where it increases drastically. After that, the normalized intensity $H / H_{\max}$ increases linearly with increasing X / L_x . As also observed from the figures, the magnetic intensity $H / H_{\max}$ is discontinuous across the hydrogel-solution interface. We may understand the phenomena above by the following two reasons: (i) the different magnetic permeabilities between the hydrogel and the surrounding fluid, and (ii) the magnetic boundary condition at the interface (3.10), which shows that the normal component of the magnetic intensity $\mathbf{H}$ is discontinuous across the material boundary [131]. Furthermore, the figures also show that no observable change is found between the magnetic field applied and magnetic field in the presence of magnetic hydrogel, when the coordinate X / L_x is far away from the hydrogel. However, they deviate from each other significantly when the coordinate X / L_x approaches the hydrogel-fluid interface, due to the prominent edge effect in the vicinity of the magnetic hydrogel [256].

Figure 4.13. Distribution of the non-dimensional magnetic field $H / H_{\max}$ along X -axis direction for the magnetic hydrogel at different times, $t = 20$ s (a), 25 s (b), and 25.1 s (c), where the solid and dash lines denote the distributions of the magnetic fields in the absence and presence of the magnetic hydrogel respectively.

4.3.2.2. *Optimization of the targeting performance of the magnetic hydrogel subject to varying magnetic intensity and magnet position*

For manipulation of the drug-loaded magnetic hydrogel in a remote manner, the external magnet may be required to vary its field strength and location in real time [123, 257]. Herein, the performance of the magnetic hydrogel is further studied subject to various magnetic stimuli, including the magnetic field strength and the field source position, in which the former is associated with the maximum magnetic intensity $H_{\max}$, and the latter with the magnet position vertically located at the coordinate $(L_D, 0)$, as illustrated in Figure 4.14(a). In the present simulation, the height of the vessel $L_V = 8 \text{ mm}$, the total height with the tissue $L_H = 10 \text{ mm}$, the other inputs of the parameters follow those in section 3.2.

Figure 4.14(b) shows the trajectories of the center point of magnetic hydrogels originally located at the coordinate $(1 \text{ mm}, 8 \text{ mm})$, when subjected to different maximum magnetic intensity $H_{\max}$, 2, 4, 6, 8, and 10 kA/m respectively, where $v_{\max} = 5 \text{ mm/s}$, $R_0 = 0.2 \text{ mm}$, and $L_D = 10 \text{ mm}$. It is seen that the hydrogel moves out of the vessel if the maximum magnetic intensity $H_{\max}$ of 2 and 4 kA/m are imposed. Because the maximum fields $H_{\max}$ of 2 and 4 kA/m are relatively weak, the motion of the hydrogel is mainly determined by the hydrodynamic effect. However, with increasing magnetic intensity $H_{\max}$, the magnetic force gradually becomes the main driving source and thus the hydrogels tend to retain at the bottom of the vessel. It is also found that, the hydrogel can be attracted to approach the magnet if $H_{\max} = 10 \text{ kA/m}$, meaning that the hydrogel-based

drug delivery system can be optimized and manipulated to the desired location by control of the external magnetic field. Moreover, It is observed from the inset of Figure 4.14(b) that, initially the hydrogel moves up slightly, and then it rises to a maximum, after which it goes down progressively. Probably the profile of the inlet flow velocity is parabolic and the initial position of the hydrogel deviates far away from the magnet, such that the hydrogels tend to move up with the hydrodynamic field at the early stage. As they move further and approach the magnet, the magnetic force increases large enough to pull them down.

Figure 4.14. Schematic of the magnetic-sensitive hydrogel placed in a moving fluid subject to a nonuniform magnetic field by a horizontally movable magnet (a). Influence of the maximum magnetic field $H_{\max}$ on trajectory of the magnetic hydrogel when $L_D = 10$ mm (b).

Figure 4.15(a) and (b) are illustrated for influence of the maximum magnetic field $H_{\max}$ on trajectories of the center point of the magnetic hydrogels subject to different magnet positions located at $L_D = 5$ and 15 mm respectively. The hydrogel tends to move toward the magnet, which demonstrates that the magnet position influences the hydrogel trajectories significantly. For example, the hydrogel travels about 4.2 mm along the horizontal direction when the magnet moves from the coordinate (5 mm, 0) to (15 mm, 0) and $H_{\max} = 6$ kA/m. This finding is in line with experimental result qualitatively [257], in which the magnetic hydrogel traveled in buffer solution following the magnetic guidance. This unique magnetic-guided directed motion is of great potential in numerous applications, such as cartilage defect therapy [257], *in vitro* cell culture [258], and microrobotic platform for therapeutic intervention [125]. Moreover, it is found from the displacement contours that, the hydrogel morphology is varied from the initial circular shape to irregular one, probably due to the inhomogeneous magnetic force and the fluid stress. For optimization of the performance of the present magnetic hydrogel for site-specific drug delivery, the magnet position is utilized as the targeting site, i.e. optimal objective. It is found that the drug-loaded hydrogels can eventually reach the targeting site via the optimization of the maximum magnetic field $H_{\max}$. When the magnet is located at the coordinate (5 mm, 0), the optimized $H_{\max}$ is attained about 24 kA/m, while it is about 7.5 kA/m for magnet at the coordinate (15 mm, 0). Therefore, it is

concluded that the magnetic-sensitive hydrogel-based drug targeting system can provide a noncontact and noninvasive platform to realize the site-specific drug delivery with desired accuracy.

Figure 4.15. Influence of the maximum magnetic field $H_{\max}$ on trajectory of the magnetic hydrogel when $L_D = 5$ mm (a), and 15 mm (b).

4.4. Remarks

This chapter elaborates the optimized designs of the magnetic-sensitive hydrogel by the MECm model in the equilibrium state, and the magnetic-sensitive hydrogel-based devices by the transient extended MECm model with the effect of moving fluid.

- For optimization of the magnetic-sensitive hydrogel, various parameter studies are carried out for influences of the magnetic properties and material parameters on behavior of the magnetic hydrogel immersed in the solvent. It is found that the swelling behavior of the magnetic hydrogel is highly associated with external uniform magnetic field, where the volume swelling ratio decreases when the magnetic induction increases. Under a nonuniform magnetic field, the instability at the long-time scale starts at a lower current and the width of hysteresis is much

smaller than that at short-time scale, and the stretch is larger at long-time scale than that at short-time scale. Furthermore, the initial swelling ratio without magnetic effect increases with decreasing volume fraction of the particles.

- For optimized design of the magnetic-sensitive hydrogel-based microfluidic flow controller, the fluid-structure interaction is characterized between the deformable magnetic hydrogel and surrounding fluid flow through the fully coupled ALE algorithm. The transient response behavior of the magnetic hydrogel is investigated, it is found that the response time for the magnetic hydrogel is improved significantly by 78% if a uniform magnetic field of 300 kA/m is applied, compared with the free swelling hydrogel without magnetic effect. Furthermore, various patterns of pulsatile flow are generated for mimicking cell physiological conditions experienced by the bone marrow stromal cells, and also for the pathological condition at the femoral artery during diastole and systole, respectively.
- Regarding the optimization of the targeting performance of the magnetic hydrogel subject to the magneto-chemo-hydro-mechanical coupled stimuli, the transient extended MECm model for suspension fluid flow in blood vessel is employed, in which a deformable magnetic-sensitive hydrogel-based drug targeting system moves with fluid. It is found that the higher flow velocity and the larger hydrogel size accelerate the movement of the hydrogel, while the smaller hydrogel size contributes to the larger swelling ratio. Furthermore, the performance of the magnetic targeting system is optimized for delivering the drug-loaded hydrogel to the desired site by variations of the maximum magnetic field strength and the magnet position.

Chapter 5. Development of a Multi-Effect-Coupling Magnetic-pH-Stimulus (MECpHm) Model for Dual Magnetic-pH-Sensitive Hydrogel

5.1. Introduction

This chapter extends the MECm model in Chapter 3 from solvent to ionic solution. Previous theoretical work in Chapter 3 only focuses on the neutral magnetic-sensitive hydrogel immersed in solvent, which is unable to characterize the performance of the charged magnetic hydrogel submerged in ionic solution. Therefore, a 3D multi-effect-coupling magnetic-pH-stimuli (MECmpH) model is developed in the present chapter for optimization of cell physiological microenvironment within the dual magnetic-pH-sensitive hydrogel-based scaffold, where the responsive mechanisms of the magnetic hydrogel in ionic solution are considered, including hydrogel magnetization, ionic polarization, diffusions of the solvent and ions, and nonlinear finite deformation, when subjected to various biophysical and biochemical stimuli, such as the magnetic field due to current intensity and the solution pH. This chapter is organized as follows. After this section, several assumptions are made and presented in Section 5.2. Section 5.3 formulates the 3D multiphysics model, and elaborates the model reduction in the equilibrium state. Section 5.4 examines the present model through two comparisons between the numerical simulation and the experimental results in open literature for the dual responsive magnetic hydrogel in response to the pH and nonuniform magnetic stimuli respectively. After that, the model is employed in Section 5.5 for two optimum designs, (i) the positions of seeding cells within the scaffold based on the threshold of mechanical force for mechanotransduction effect at cellular-size level, and (ii) the

concentration of potassium (K^+) within the scaffold based on the common biological requirement for the cell growth. Finally, several remarks are given in Section 5.6.

5.2. Assumptions

For theoretical formulation of the model in Lagrangian scheme, several assumptions are made in detail:

- The magnetic-pH-sensitive hydrogel system remains at the isothermal condition, such that the dissociation constant K_d is independent of temperature
- The magnetic particles are immobilized and dispersed homogeneously within the hydrogel.
- The present hydrogel has the macroporous property, and thus the diffusivity constant of the mobile ions D_k remains the same over the domains covering both the hydrogel and environmental solution.

5.3. Formulation of the MECmpH model

In this section, the responsive mechanisms of the magnetic-pH-sensitive hydrogel are characterized by the mathematic description of the hydrogel magnetization, ionic polarization, solvent and ions diffusions, and the hydrogel large deformation.

As shown in Figure 5.1, the present magnetic-pH-sensitive hydrogel is a combination of anionic hydrogel embedded with magnetic particles at micro- or nano-level, such as $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4 , and CoFe_2O_3 , that can react to external magnetic field and the change of solution pH at the same time [259]. The external solution is comprised of four species, solvent molecules (i.e. water), hydrogen ions, co-ions that have the same charge as the

fixed charge (i.e. chloride ions), and the counterions that have the opposite charge to the fixed charge (i.e. sodium ions). If the hydrogel is submerged in bath solution, some functional groups in the polymeric chain dissociate, leading to the formations of the mobile ions and the fixed charges attached to the chain. Due to the fixed charges, the ionic concentration differs between the interior hydrogel and the exterior solution. As a result, an osmotic pressure is generated and it contributes to the swelling or deswelling of the hydrogel. Simultaneously, if an external magnetic field is employed, two distinct interactions may occur, particle-particle and field-particle interactions, due to the magnetic particle magnetization and the magnetic field gradient respectively [131]. Since the particles are tightly anchored into the flexible network chain, the movement of the particles further drives the deformation of the hydrogel [90], which in turn redistributes the magnetic field, diffusive mobile ions, as well as fixed charge groups. Therefore, it is a full-loop magneto-chemo-electric-mechanical coupled system.

Figure 5.1. Schematic of a cylindrical magnetic-pH-sensitive hydrogel placed in bath solution subject to a nonuniform magnetic field generated by an electromagnet.

5.3.1. Governing equations

5.3.1.1. Magnetic field

In accordance with the equations for magnetostatics from (3.6) to (3.10), the distributive magnetic field in Lagrangian coordinate $\mathbf{X}$ is governed by the Maxwell's equations

$$\nabla_{\mathbf{X}} \times \mathbf{H} = 0, \quad \nabla_{\mathbf{X}} \cdot \mathbf{B} = 0 \quad (5.1)$$

where the magnetic induction $\mathbf{B}$ and intensity $\mathbf{H}$ are associated with magnetization vector $\mathbf{M}$ by

$$\mathbf{B} = \mu_0 J \mathbf{C}^{-1} (\mathbf{H} + \mathbf{M}) \quad (5.2)$$

Across the hydrogel-solution interface $\partial\beta_0$, they are required to satisfy the jump conditions

$$\mathbf{N} \cdot [[\mathbf{B}]] = 0, \quad \mathbf{N} \times [[\mathbf{H}]] = 0 \quad (5.3)$$

5.3.1.2. Electric field

By the Gauss's theorem [260], the distributive electric displacement $\mathbf{D}$ in hydrogel and surrounding solution satisfies the equation below

$$\nabla_{\mathbf{X}} \times \mathbf{E} = 0, \quad \nabla_{\mathbf{X}} \cdot \mathbf{D} = F_r (z_f C_f + \sum_k z_k C_k) \quad (5.4)$$

where $\mathbf{E}$ denotes the electric field strength, z_f and C_f are the valence and concentration of the fixed charges, z_k and C_k the valence and concentrations of the mobile ions, and F_r the Faraday's constant.

Across the hydrogel-solution interface $\partial\beta_0$, the vectors of electric field strength $\mathbf{E}$ and displacement $\mathbf{D}$ are required to satisfy the jump conditions

$$\mathbf{N} \cdot [[\mathbf{D}]] = 0, \quad \mathbf{N} \times [[\mathbf{E}]] = 0 \quad (5.5)$$

5.3.1.3. Chemical field for diffusions of solvent and ions

Based on the conservation of mass [207], the chemical field with respect to the solvent diffusion is written in the local form of

$$\dot{C}_s = -\nabla_{\mathbf{x}} \cdot \mathbf{J}_s + R_s \quad (5.6)$$

where $C_s(\mathbf{X}, t)$ denotes the concentration of solvent, $\mathbf{J}_s$ the solvent flux, and R_s the rate of solvent generation by chemical reaction.

Similarly, the chemical field with respect to the ionic diffusion is expressed as

$$\dot{C}_k = -\nabla_{\mathbf{x}} \cdot \mathbf{J}_k + R_k \quad (5.7)$$

where C_k , $\mathbf{J}_k$, and R_k are ion concentration, flux, and generation for the k th mobile species respectively.

5.3.1.4. Mechanical field

For incorporation of the mechanical effect into the hydrogel response, the mechanical equilibrium with nonlinear large mechanical deformation is employed as [131]

$$\rho_0 \dot{\mathbf{V}}_h = \nabla_{\mathbf{x}} \cdot \mathbf{P} + \rho_0 \mathbf{f}_b \quad (5.8)$$

where ρ_0 is the mass density of the polymer network, $\mathbf{V}_h$ the deformation velocity, $\mathbf{P}$ the Piola stress tensor, and $\mathbf{f}_b$ the external force density.

5.3.2. Constitutive equations

To formulate the equations of state for present hydrogel system with large deformation at isothermal condition, the free energy imbalance inequality is employed by [206]

$$\frac{d}{dt} \left\{ \int_{V_0} \left(\Psi + \frac{1}{2} \rho_0 |\mathbf{V}_h|^2 \right) dV_0 \right\} \leq \dot{W} + \dot{C} + \dot{E} + \dot{M} \quad (5.9)$$

where Ψ is the free energy density, and $\dot{W}$ the mechanical power contributed by the traction force $\mathbf{t} = \mathbf{P}\mathbf{N}$ and the force $\mathbf{f}_b$ acting on the hydrogel, namely

$$\dot{W} = \int_{S_0} \mathbf{P}\mathbf{N} \cdot \mathbf{V}_h dS_0 + \int_{V_0} \rho_0 \mathbf{f}_b \cdot \mathbf{V}_h dV_0 \quad (5.10)$$

The chemical power $\dot{C}$ may vary due to the solvent and ionic diffusions, and the mass generation R_s and R_k via chemical reaction. Hence, the power $\dot{C}$ is written as [2, 261]

$$\dot{C} = - \int_{S_0} \mu_s \mathbf{J}_s \cdot \mathbf{N} dS_0 + \int_{V_0} \mu_s R_s dV_0 - \sum_k \left(\int_{S_0} \mu_k \mathbf{J}_k \cdot \mathbf{N} dS_0 - \int_{V_0} \mu_k R_k dV_0 \right) \quad (5.11)$$

where μ_s and μ_k are the solvent and ionic chemical potentials respectively.

The power $\dot{E}$ due to the electric field is expressed as [262]

$$\dot{E} = \int_{V_0} (\mathbf{E} \cdot \dot{\mathbf{D}} - F_r \phi \sum_k z_k \dot{C}_k) dV_0 \quad (5.12)$$

where ϕ and $\mathbf{E}$ are the electric potential and electric intensity respectively.

In general, the magnetic power $\dot{M}$ is mainly contributed by two components, one is associated with the magnetization of the magnetic hydrogel [43], and the other one related to the magnetic migration effect on the mobile ions [263]. Consequently, we have

$$\dot{M} = \int_{V_0} (\mathbf{H} \cdot \dot{\mathbf{B}} - F_r L \sum_k z_k \dot{C}_k) dV_0 \quad (5.13)$$

where $L = \mathbf{v} \cdot \mathbf{A}$ is the potential of the ion species k (Here $\mathbf{B} = \nabla \times \mathbf{A}$), and it satisfies the relation $\mathbf{v} \times \mathbf{B} = -\nabla L$.

By sum of Equations (5.10) to (5.13), with the aid of the mass and mechanical balance equations (5.6)-(5.8) and the divergence theorem, the local form of the inequality (5.9) is rewritten as

$$\begin{aligned} \dot{\Psi} \leq & \mathbf{P} : \dot{\mathbf{F}} + \mu_s \dot{C}_s + \sum_k \mu_k \dot{C}_k - \mathbf{J}_s \cdot \nabla_{\mathbf{x}} \mu_s - \sum_k (\mathbf{J}_k \cdot \nabla_{\mathbf{x}} \mu_k) \\ & + \mathbf{H} \cdot \dot{\mathbf{B}} - F_r L \sum_k z_k \dot{C}_k + \mathbf{E} \cdot \dot{\mathbf{D}} - F_r \phi \sum_k z_k \dot{C}_k \end{aligned} \quad (5.14)$$

If Helmholtz free energy density Ω is a function of state depending on the five independent variables, namely the magnetic induction $\mathbf{B}$, the electric displacement $\mathbf{D}$, the concentrations of solvent C_s and ions C_k , as well as the deformation gradient $\mathbf{F}$, we have

$$\begin{aligned}
& \left(\frac{\partial \Psi}{\partial \mathbf{F}} - \mathbf{P} \right) : \dot{\mathbf{F}} + \left(\frac{\partial \Psi}{\partial \mathbf{B}} - \mathbf{H} \right) \cdot \dot{\mathbf{B}} + \left(\frac{\partial \Psi}{\partial \mathbf{D}} - \mathbf{E} \right) \cdot \dot{\mathbf{D}} + \left(\frac{\partial \Psi}{\partial C_s} - \mu_s \right) \dot{C}_s \\
& + \sum_k \left[\frac{\partial \Psi}{\partial C_k} - \mu_k + F_r(\phi + L)z_k \right] \dot{C}_k + \mathbf{J}_s \cdot \nabla_{\mathbf{x}} \mu_s + \sum_k \mathbf{J}_k \cdot \nabla_{\mathbf{x}} \mu_k \leq 0
\end{aligned} \tag{5.15}$$

The coefficient in any bracket vanishes, the arbitrariness of the variables, such that the constitutive equations are given below

$$\mathbf{P} = \frac{\partial \Psi}{\partial \mathbf{F}}, \quad \mathbf{H} = \frac{\partial \Psi}{\partial \mathbf{B}}, \quad \mathbf{E} = \frac{\partial \Psi}{\partial \mathbf{D}}, \quad \mu_s = \frac{\partial \Psi}{\partial C_s}, \quad \mu_k = \frac{\partial \Psi}{\partial C_k} + F_r(\phi + L)z_k \tag{5.16}$$

To ensure the inequality held, the solvent flux $\mathbf{J}_s$ and the ionic flux $\mathbf{J}_k$ are associated with the chemical potential gradient $\nabla_{\mathbf{x}} \mu_s$ and $\nabla_{\mathbf{x}} \mu_k$ respectively via [211]

$$\mathbf{J}_s = -\frac{C_s D_s \mathbf{C}^{-1}}{k_B T} \nabla_{\mathbf{x}} \mu_s, \quad \mathbf{J}_k = -\frac{C_k D_k \mathbf{C}^{-1}}{k_B T} \nabla_{\mathbf{x}} \mu_k \tag{5.17}$$

where $k_B T$ is the temperature in the unit of energy, D_s and D_k the diffusion coefficients of solvent and ions respectively.

5.3.3. Free energy density

To characterize the performance of the magnetic hydrogel, an explicit free energy density Ψ is required, where five components are considered, including the stretching of the polymer networks Ψ_{ela} , the mixing of the polymers and solvent Ψ_{sol} , the mixing of the solvent and ions Ψ_{ion} , the magnetization Ψ_{mag} , and the polarization Ψ_{ele} . Based on the Flory-Rehner theory, the energy density Ψ_{ela} and Ψ_{mix} with the effect of volume fraction of the magnetic particles ξ_p are given respectively by [131, 216, 264]

$$\Psi_{ela} = \frac{1}{2} G \{ \text{tr}(\mathbf{F}^T \mathbf{F}) - 3 - 2 \ln[\det(\mathbf{F})] \} \quad (5.18)$$

$$\Psi_{sol} = \frac{k_B T}{v_s} [v_s C_s \ln(\frac{v_s C_s + \xi_p}{\det(\mathbf{F})}) + \chi_H v_s C_s \frac{1 - \xi_p}{\det(\mathbf{F})}] \quad (5.19)$$

where G is the hydrogel shear modulus, v_s the volume per solvent species, ξ_p the volume fraction of magnetic particles, and χ_H the Flory-Huggins parameter to characterize the interaction between the polymer network and solvent.

The free energy density owing to the mixing between the solvent and mobile ions is described by [262]

$$\Psi_{ion} = k_B T \sum_k C_k (\ln C_k - \ln C_s - 1) \quad (5.20)$$

The free energy densities of magnetization Ψ_{mag} and polarization Ψ_{ele} for an ideal hydrogel in reference configuration are generally given in the form of [233]

$$\Psi_{mag} = \frac{\mathbf{B} \cdot \mathbf{CB}}{2\mu_0 \mu_{mr} J}, \quad \Psi_{ele} = \frac{\mathbf{D} \cdot \mathbf{CD}}{2\varepsilon_0 \varepsilon_{er} J} \quad (5.21)$$

where ε_{er} and μ_{mr} are the relative permittivity and magnetic permeability, ε_0 is the dielectric permittivity in vacuum.

By sum of Equations (5.18) to (5.21), and accounting for the molecular incompressibility condition $1 + v_s C_s = \det(\mathbf{F})$ for hydrogel in dilute solution [205, 211], the free energy density Ω is given below

$$\begin{aligned} \Psi = & \frac{1}{2} G \{ \text{tr}(\mathbf{F}^T \mathbf{F}) - 3 - 2 \ln[\det(\mathbf{F})] \} + \frac{k_B T}{v_s} [v_s C_s \ln(\frac{v_s C_s + \xi_p}{1 + v_s C_s}) + \chi_H v_s C_s \frac{1 - \xi_p}{1 + v_s C_s}] \\ & + \frac{\mathbf{D} \cdot \mathbf{CD}}{2 \varepsilon_0 \varepsilon_{er} J} + \frac{\mathbf{B} \cdot \mathbf{CB}}{2 \mu_0 \mu_{mr} J} + k_B T \sum_k C_k (\ln C_k - \ln C_s - 1) + \Pi [1 + v_s C_s - \det(\mathbf{F})] \end{aligned} \quad (5.22)$$

where Π is the Lagrange multiplier and also interpreted as the osmotic pressure [211, 217].

From the free energy density equation (3.62) and the constitutive equation (5.16), the magnetic intensity $\mathbf{H}$, the electric intensity $\mathbf{E}$, the chemical potential μ_k and μ_s , and the stress $\mathbf{P}$ are expressed respectively as

$$\mathbf{H} = \mathbf{CB} / (\mu_0 \mu_r J) \quad (5.23)$$

$$\mathbf{E} = \mathbf{CD} / (\varepsilon_0 \varepsilon_r J) \quad (5.24)$$

$$\mu_k = k_B T \ln \frac{C_k}{C_s} + F_r (\phi + L) z_k \quad (5.25)$$

$$\mu_s = k_B T \left[\ln \left(\frac{v C_s + \xi_p}{1 + v C_s} \right) + \frac{1 - \xi_p}{1 + v C_s} + \chi_H \left(\frac{1 - \xi_p}{1 + v C_s} \right)^2 \right] - \frac{k_B T \sum_k C_k}{C_s} + \Pi v_s \quad (5.26)$$

$$\mathbf{P} = G(\mathbf{F} - \mathbf{F}^{-T}) - \Pi \mathbf{F}^{-T} + \frac{(\mathbf{FD}) \otimes \mathbf{D}}{\varepsilon_0 \varepsilon_{er} J} - \frac{\mathbf{D} \cdot \mathbf{CD}}{2 \varepsilon_0 \varepsilon_{er} J} \mathbf{F}^{-T} + \frac{(\mathbf{FB}) \otimes \mathbf{B}}{\mu_0 \mu_{mr} J} - \frac{\mathbf{B} \cdot \mathbf{CB}}{2 \mu_0 \mu_{mr} J} \mathbf{F}^{-T} \quad (5.27)$$

On the basis of the Faraday's law, the magnetic intensity $\mathbf{H}$ is defined as a function of the magnetic scalar potential ψ by $\mathbf{H} = -\nabla_{\mathbf{x}} \psi$, and the electric intensity $\mathbf{E}$ relates to the electric potential ϕ via $E = -\nabla_{\mathbf{x}} \phi$. By Equations (5.1) and (5.23), the magnetic potentials ψ in both the magnetic hydrogel and the exterior solvent are rewritten as

$$\nabla_{\mathbf{x}} \cdot (J\mu_0\mu_{mr}\mathbf{C}^{-1}\nabla_{\mathbf{x}}\psi) = 0 \quad (5.28)$$

and by Equations (5.4) and (5.24), the electric potentials ϕ in both the magnetic hydrogel and the exterior solution are rewritten as

$$\nabla_{\mathbf{x}} \cdot (J\epsilon_0\epsilon_{er}\mathbf{C}^{-1}\nabla_{\mathbf{x}}\phi) = -F_r(z_f C_f + \sum_k z_k C_k) \quad (5.29)$$

where the fixed charge density of anionic hydrogel C_f describes the interaction between the fixed charge groups and mobile ions, and it is given by the Langmuir monolayer adsorption theory [265] as

$$C_f = \frac{\phi_s^0 C_f^0 J K_d}{J K_d + C_{H^+}} \quad (5.30)$$

where ϕ_s^0 denotes the volume fraction of the polymeric network at reference state, K_d the dissociation constant, C_{H^+} the hydrogen ion concentration, as well as C_f^0 the concentration of fixed charges at dry state.

5.3.4. Model reduction in the equilibrium state

Based on Equations (5.6) and (5.25), if no chemical reaction occurs for generation of extra ionic species, the ion transport in the equilibrium state is given by

$$\nabla_{\mathbf{x}} \cdot \left[D_k \mathbf{C}^{-1} \left(\nabla_{\mathbf{x}} C_k + \frac{z_k C_k F_r}{k_B T} (\nabla_{\mathbf{x}} \phi - \mathbf{v} \times \mathbf{B}) \right) \right] = 0, \quad (5.31)$$

It is found that the diffusion of the mobile ions is dependent on three driving forces, namely the concentration gradient, electric force, and magnetic effect, and the diffusion equation developed by the present model is consistent with the theoretical work [266] for magnetohydrodynamic flow of RedOx electrolyte subject to the electric and magnetic fields. When the hydrogel is immersed in an unstirred solution, the ion diffusion due to convection can be neglected, namely the induction term $\mathbf{v} \times \mathbf{B}$ is not considered in the subsequent analysis.

For the mechanical equilibrium of the hydrogel system, Equation (5.8) is rewritten as

$$\nabla_{\mathbf{x}} \cdot \mathbf{P} = 0 \quad (5.32)$$

if the external body force $\mathbf{f}_b$ is neglected and only the equilibrium state is considered.

Under equilibrium conditions, the chemical potentials of solvent and ions in the hydrogel coincide with those in bath solution, namely

$$\mu_s = \bar{\mu}_s, \mu_{H^+} = \bar{\mu}_{H^+}, \mu_+ = \bar{\mu}_+, \mu_- = \bar{\mu}_- \quad (5.33)$$

where the overbar denotes the parameters in the surrounding solution. Insertions of Equation (5.26) into (5.33), the osmotic pressure Π is obtained as

$$\begin{aligned} \Pi = & -\frac{k_B T}{v_s} \left(\ln \left(\frac{vC_s + \xi_p}{1 + vC_s} \right) + \frac{1 - \xi_p}{1 + vC_s} + \chi_H \left(\frac{1 - \xi_p}{1 + vC_s} \right)^2 \right) \\ & + \frac{k_B T}{v_s} \left(\frac{C_{H^+} + C_+ + C_-}{C_s} - \frac{\bar{C}_{H^+} + \bar{C}_+ + \bar{C}_-}{\bar{C}_s} \right) \end{aligned} \quad (5.34)$$

$$C_{H^+} = \bar{C}_{H^+}, C_+ = \bar{C}_+, C_- = \bar{C}_-, \phi = 0, \psi = \psi(R, Z) \quad \text{at } \partial S_0 \quad (5.36)$$

where the magnetic boundary condition $\psi = \psi(R, Z)$ is constructed from the measured magnetic field along the axial direction by Equation (5.28).

At the hydrogel-solution interface $\partial\beta_0$, we have the following mechanical boundary condition,

$$\mathbf{P} \cdot \mathbf{N} = \mathbf{T}_m + \mathbf{T}_e \quad \text{at } \partial\beta_0 \quad (5.37)$$

where $\mathbf{T}_m$ and $\mathbf{T}_e$ are the magnetic and electric tractions acting on the boundary $\partial\beta_0$ ($\mathbf{T}_m = \mathbf{P}_m \cdot \mathbf{N}$ and $\mathbf{T}_e = \mathbf{P}_e \cdot \mathbf{N}$), here the Maxwell stress $\mathbf{P}_m$ and $\mathbf{P}_e$ are defined respectively as

$$\mathbf{P}_m = \mathbf{F}^{-T} (\mathbf{H} \otimes \mathbf{B}) - \frac{1}{2} (\mathbf{H} \cdot \mathbf{B}) \mathbf{F}^{-T}, \quad \mathbf{P}_e = \mathbf{F}^{-T} (\mathbf{E} \otimes \mathbf{D}) - \frac{1}{2} (\mathbf{E} \cdot \mathbf{D}) \mathbf{F}^{-T} \quad (5.38)$$

So far the MECmpH model has been completed theoretically for the magnetic-sensitive hydrogel placed in ionic solution under coupled magneto-chemo-electro-mechanical fields. In the equilibrium state, the governing equations are comprised of magnetostatic equation (5.28), electrostatic equation (5.29), ionic diffusion equation (5.31), and mechanical equilibrium equation (5.32). Furthermore, the free energy density is specified via Equation (3.62), and the corresponding constitutive behavior characterized by Equations (5.23) to (5.27). For simulation of the hydrogel performance, the finite element package COMSOL Multiphysics 5.3 is used, as a result of its ability in solving the coupled nonlinear partial differential equations with desired accuracy.

5.4. Validations of the MECmpH model

5.4.1. Equilibrium swelling of HEMA hydrogel

For validation of the MECmpH model, a comparison is carried out with the experimental result [267], where the hydrogel was synthesized by the homogeneous copolymers of acrylic acid and hydroxyl-ethyl-methacrylate acid (HEMA) with the diacrylate crosslinker. The axial displacement of the cylindrical hydrogel was constrained by the cover glasses positioned at the two ends, such that the hydrogel with radius R_0 of 250 μm only swelled in the radial direction. In the present simulation, it is reasonable to employ the 2D MECmpH model to estimate the hydrogel response in the equilibrium state, when it is placed in a bath solution with an ionic strength of 300 mM and subjected to the varying solution pH. The inputs required for the MECmpH model are tabulated in Table 5.1. It is worth noting that, the shear modulus G varies in a trilinear form [267], At low $\text{pH} < 5.5$, the hydrogel remains almost constant shear modulus $G = 101.4 \text{ kPa}$, whereas it decreases to another constant $G = 80.4 \text{ kPa}$ if $\text{pH} > 7.5$. At the intermediate pH range from 5.5 to 7.5, the linear decrease of shear modulus G is obtained.

Table 5.1. Input parameters for validation of the MECmpH model.

parameters	symbol	value
initial fixed charge density	C_f^0	1800 mM [267]
external concentration of Na^+	$\bar{C}_{\text{Na}^+}$	300 mM [267]
external concentration of Cl^-	$\bar{C}_{\text{Cl}^-}$	300 mM [267]
external concentration of H^+	$\bar{C}_{\text{H}^+}$	$10^{(3-\text{pH})} \text{ mM}$
diffusion coefficient of Na^+	D_{Na^+}	$1.3 \times 10^{-9} \text{ m}^2/\text{s}$ [268]

diffusion coefficient of Cl^-	D_{Cl^-}	$2.032 \times 10^{-9} \text{ m}^2/\text{s}$ [268]
diffusion coefficient of H^+	D_{H^+}	$9.31 \times 10^{-9} \text{ m}^2/\text{s}$ [268]
dissociation constant	K_d	0.01 mM [267]
Faraday's constant	F	$1.603 \times 10^{-19} \text{ C}$
dielectric permittivity in vacuum	ϵ_0	$8.8542 \times 10^{-12} \text{ F/m}$
relative dielectric permittivity	ϵ_{er}	80 [197]
temperature in the unit of energy	$k_B T$	$4.11 \times 10^{-21} \text{ J}$

Figure 5.3 is plotted for comparison between the present simulation and the published experimental result for the deformation of the HEMA hydrogel placed in bath solution at various pH levels. To examine the predictive capability of the model, the global error δ is calculated by $\delta = \sqrt{\sum_{i=0}^N (u_i - u_i^e)^2 / n} / |u_{\max}|$ [269], where n is the number of experimental points, u_i and u_i^e are the simulation results and the corresponding experimental data, and $|u_{\max}|$ is the maximum absolute value of the simulation results. Hence, the global error $\delta = 1.87\%$ is achieved, such that the present model enables to predict the hydrogel behavior with desired accuracy. As also seen from the figure, the solution pH has a pronounced effect on variation of the hydrogel deformation. The diameters of the HEMA hydrogel remain about 570 and 1100 μm when $\text{pH} < 4$ and $\text{pH} > 7$ respectively, whereas the hydrogel undergoes an abrupt change in the pH value ranging from 4 to 7. The pH-induced hydrogel swelling may be attributed to pendant acidic groups on the backbone of the network. The acidic group is slightly ionized when the solution pH is far below the pKa value of the HEMA hydrogel ($\text{pKa} = 4.7$), resulting in a minimal swelling of the hydrogel. However, when the

environmental pH rises to approach the hydrogel pKa, the acidic groups are remarkably ionized, resulting in a sharp increase of the fixed charge density C_f . In general, the increase of fixed charge density C_f in the acidic hydrogel contributes to diffusion of mobile ions with positive charges [270]. The associated increase of the ionic concentration in the interior hydrogel generates a large osmotic pressure, which induces an observable increase in swelling. If the ionization degree reaches the saturation point at about pH = 7, no noticeable change is found in the swelling of the HEMA hydrogel, if solution pH increases further.

Figure 5.3. Comparison of the present theoretical simulation and published experiment for deformation of the HEMA hydrogel with the solution pH ranging from 2 to 12.

5.4.2. Deformation of PVA magnetic hydrogel

For further validation, the simulated equilibrium deformation of the magnetic hydrogel is compared with the published experimental data [88], where a cylindrical magnetic hydrogel was prepared via the chemically crosslinked PVA polymer and magnetic particles (Fe_3O_4), and it was immersed in water under a nonuniform magnetic field. To describe the hydrogel response, the boundary condition is required on the magnetic scalar

potential $\psi = \psi(R, Z)$ at the exterior solution edge ∂S_0 . In this validation, it is reconstructed from the experiment on the magnetic field along the axial direction [88]. In the absence of the magnetic hydrogel, the magnetic induction divided by the current intensity $B(0, Z)/I$ was tested experimentally as a function of the distance Z from the surface of the electromagnet, which is fitted by a fifth-degree polynomial, $B/I = 60.4934 Z^5 - 4.8576 Z^4 - 9.6825 Z^3 + 2.9074 Z^2 - 0.3136 Z + 0.0124$, as shown in Figure 5.4(a). It is noted that the maximum magnetic field $H_{\max}$ on top surface of the electromagnet is associated with the current intensity I by $H_{\max} = 9946.8I$ A/m. According to the relation $\mathbf{H} = -\nabla_{\mathbf{x}}\psi$, the magnetic scalar potential ψ is written as a sixth-degree polynomial $\psi(0, Z) = p_6(Z)$. Moreover, the distribution of the magnetic scalar potential ψ in the solution satisfies the Laplace's equation $\nabla_{\mathbf{x}}^2 \psi = 0$ (5.28). Therefore, the analytical solution of the magnetic potential ψ is given by $\psi(R, Z) = p_6(Z) - R^2 p_6^{(2)}(Z)/4 + R^4 p_6^{(4)}(Z)/64 - R^6 p_6^{(6)}(Z)/2304$ [243], which is imposed on the solution boundary ∂S_0 . The input parameters for the validation include: $L_R = 80$ mm, $L_H = 200$ mm, $r_0 = 7$ mm, $h_0 = 122.1$ mm, $z_0 = 24.2$ mm, $G = 1$ kPa, and $\mu_{mr} = 1.14$. Figure 5.4(b) illustrates the comparison of the present numerical simulation with the experimental data [88] for the magnetic field-induced hydrogel length change Δh . The deformation Δh increases with the increase of the current intensity I , due to the stronger magneto-elastic effect. Furthermore, the simulated results agree well with the experimental finding, where a global error of 3.39% is obtained for the comparison. It

then further indicates the validity of the present MECmpH model, such that it is reasonable to utilize the model to undertake the studies below.

Figure 5.4. (a) Fitting curve of the experimental measurement on magnetic field distribution along axial direction [88] by a fifth-degree polynomial. (b) Comparison of the present theoretical simulation (solid line) and the experiment [88] (square brick) for the magnetic field-dependent deformation of the magnetic hydrogel.

5.5. Optimization of the cell microenvironment within the magnetic scaffold

It is known that the physiological processes including cell metabolism, mass transfer, and tissue growth are highly dependent on the synergistic effects of biophysical (e.g. mechanical force) and biochemical factors (e.g. ionic concentration) [130]. Herein, a dual magnetic-pH-sensitive hydrogel-based scaffold is designed and optimized by the MECmpH model to delivers suitable biophysical and biochemical cues to regulate cell behaviors when subjected to the magnetic and pH coupled stimuli. In this section, two optimizations are conducted, (i) the positions of seeding cells within the scaffold based on the threshold of mechanical force for mechanotransduction effect at cellular-size level, and (ii) the concentration of potassium (K^+) within the scaffold based on the common biological requirement for the cell growth.

5.5.1. Mechanical response of the magnetic scaffold

To understand the mechanical stimulation on the cells by the scaffold deformation in response to the magnetic and pH coupled stimuli, it is essential to characterize the distributive magnetic field and the coupled field-induced nonlinear deformation. Based on the literature survey in Chapter 2, no effort was made to investigate the magneto-chemo-electro-mechanical behavior of the magnetic hydrogel. Thereby, the validated MECmpH model is utilized for the first time to study the mechanical responsive behavior of the magnetic scaffold. It is commonly known that the magnetic field distributions in both the hydrogel and solution domains are associated with the hydrogel-magnet distance z_0 [88, 271] and the maximum magnetic field due to the current intensity I applied to the electromagnet [88], such that the two key factors are considered here to study the mechanical behavior of the magnetic scaffold. As well known, the physiological pH of the human body approximates 7.4 and exhibits pronounced differences among the organs, such as the stomach with gastric fluid (i.e. pH 1.5~3.5), the bladder with urine (i.e. pH 4.6~8), and tumor tissue (i.e. pH 4.5~6) [116]. Herein, the anionic magnetic hydrogel-based scaffold works in bath solution with pH ranging from 4 to 8 and with the ions of Na^+ , H^+ , Cl^- , and OH^- at physiological condition [198]. To obtain the impact of the mechanical effect on the cells within the scaffold due to the scaffold deformation, the stimulation force F_m is estimated by the Hooke's law: $F_m = EA_0\Delta h/h_0$ [50], where E is the cell Young's modulus, A_0 the original cross-sectional area. The original nonuniform magnetic field generated by the external electromagnet follows that in Figure 5.4(a). The inputs required by the model include: $C_f^0 = 100 \text{ mM}$, $\bar{C}_{\text{Na}^+} = \bar{C}_{\text{Cl}^-} = 150 \text{ mM}$, $r_0 = 4 \text{ mm}$, $h_0 = 4 \text{ mm}$, $E = 7 \text{ kPa}$, $A_0 = 10^{-10} \text{ m}^2$, $G = 100 \text{ kPa}$, and $\xi_p = 0.15$, and the other

inputs are obtained from Table 5.1. It is worth mentioning that the parameters are obtained from the open literature [50, 198, 257, 272], for the hydrogel at the physiological state, such that the *in vivo* performance of the magnetic scaffold can be characterized by the MECmpH model.

Figure 5.5 (a) and (b) show the effect of the surrounding pH level on variation of the mechanical force F_m exerted on cells adhered on top surface of the scaffold against current intensity I , when subjected to varying hydrogel-magnet distance z_0 , 2 and 8 mm respectively. The mechanical force F_m increases with the increasing current intensity I , and it further increases with the increase of the solution pH. It is because that the acidic functional group is ionized more with the increasing pH, which yields a larger osmotic pressure and thus drives the larger scaffold deformation. It is also found from Figure 5.5(a) that the mechanical force F_m acting on cells is about 4.6 pN when the current intensity $I = 0.14$ A and pH = 4, whereas the force F_m decreases around 1.4 times accordingly, as illustrated in Figure 5.5(b). Probably the magnitude of the magnetic field decays away from the electromagnet and thus the magnetic field-induced scaffold deformation decreases with increasing hydrogel-magnet distance z_0 . Thereby, it is worthwhile to characterize the distribution of magnetic field for optimization of magnetic hydrogel-based scaffold.

Figure 5.5. Influence of the solution pH on variation of the mechanical force on cells adhered to the hydrogel top surface against the current intensity I , when subjected to different hydrogel-magnet distance $z_0 = 2$ mm (a), and 8 mm (b).

Figure 5.6 presents the magnetic field distribution along the coordinate $R = 0$ in the presence of magnetic hydrogel at the distances z_0 of 2, 4, 6, and 8 mm respectively. As observed from the figure that, the non-dimensional magnetic field $H/H_{\max}$ decreases with increasing non-dimensional coordinate Z/L_H , it then increases to a maximum at the hydrogel-solution interface, where the field $H/H_{\max}$ follows a step function with a sharp decrease at the interface within a small range of the normalized coordinate Z/L_H . Subsequently, it rises up to another maximum and then decreases until it reaches the interface again, where it increases drastically. Moreover, it is found that the magnetic field $H/H_{\max}$ is discontinuous across the hydrogel-solution interface. We may understand the phenomena above by the following two reasons: (i) the different magnetic permeabilities between the hydrogel and the bath solution, and (ii) the magnetic boundary condition at the interface (5.3), demonstrating that the tangential component of the magnetic intensity $\mathbf{H}$ is continuous across the material boundary, whereas the normal

component of the magnetic intensity $\mathbf{H}$ is discontinuous across the material boundary [131]. Furthermore, as is seen from the inset of the figure, the non-dimensional magnetic field strength $H/H_{\max}$ at the coordinate $Z/L_H = 0$ increases greatly from 1.005 to 1.114 when the hydrogel-magnet distance z_0 decreases from 8 to 2 mm. Because the original magnetic field applied is distorted by adding the magnetic hydrogel and the distortion is more obvious when the hydrogel approaches the magnet. This phenomenon is referred to as edge effect [256], which plays an important role in design and optimization of magnetic material based devices [273].

Figure 5.6. Influence of the hydrogel-magnet distance z_0 on variation of the non-dimensional magnetic field distribution $H/H_{\max}$ along the vertical line located at $R = 0$.

In general, the magnetic scaffold may undergo an inhomogeneous deformation due to the local gradient field by a nonuniform magnetic stimulus [43]. As the cells are tightly attached to the scaffold, the inhomogeneous scaffold deformation may induce the variation of the mechanical forces on cells at different seeding position. It is reported from the literature that the mechanical force of 0.2 pN was required to activate the

TREK-1 channel [274], while 2 pN may break the molecular slip bond between fibronectin and the cytoskeleton [275]. In addition, the range of 0.2~2 pN was used as the threshold of mechanical force for mechanotransduction effect at cellular-size level, under which the mechanic-sensitive receptors were activated, initiating biochemical pathways to produce the mature tissue [50, 271]. Therefore, the range of 0.2~2 pN is also adopted in the present optimization for cell mechanical microenvironment.

Figure 5.7. Influence of the current intensity I on variation of the distribution of the mechanical force F_m on cells adhesive to the magnetic scaffold, where $\text{pH} = 6$, $z_0 = 6$ mm, and $I = 0.024\text{A}$ (a), 0.028A (b), 0.076A (c), and 0.084A (d).

Figure 5.7 demonstrates the impact of the current intensity I on distribution of the mechanical force F_m exerted on the cells, where the solution $\text{pH} = 6$ and $z_0 = 6$ mm . As

observed from Figure 5.7(a), the force F_m is less than 0.2 pN if the current intensity $I = 0.024 \text{ A}$, where the weak stimulation force may be insufficient to activate the mechanosensitive ion channel in the cells. When the current I increases from 0.024 to 0.028A, the force F is still less than 0.2 pN if cells are seeded at the upper region of the scaffold, while it is larger than 0.2 pN if the cells are seeded at the lower region of the scaffold, as illustrated in Figure 5.7(b). It is noted that the upper and lower regions in the contour are separated by a black curve for the force $F_m = 0.2 \text{ pN}$. It is also found that the force increases with the increasing coordinate R , when the axial coordinate Z is fixed (i.e. $Z = 0.012 \text{ m}$). The magnetic field-induced inhomogeneous deformation at the centerline of the scaffold (i.e. $R = 0$) is the smallest, showing good agreement with the published experimental findings qualitatively [276]. Probably the magnitude of the magnetic force F_f is associated with local magnetic field via $F_f = \mu_0(\mu_{mr} - 1)(H_t^2 + \mu_r H_n^2)/2$ [241], where H_t and H_n are the tangential and normal components of the magnetic fields over the hydrogel-solution interface respectively. Although the normal component of the magnetic field H_n decreases with the increasing coordinate R , the tangential one H_t increases gradually. Consequently, the magnetic force and the force-induced deformation at the larger coordinate R may exceed that at the center. Regarding the case of the current intensity $I = 0.076 \text{ A}$, the cells may be seeded at any region of the scaffold since the force F_m is distributed in the optimized range of $0.2 \sim 2 \text{ pN}$, as shown in Figure 5.7(c). However, when the current intensity I increases further from 0.076 to 0.084A, the cell structure may be broken [50], since the force F_m is larger than 2 pN if the cells are seeded at the lower region of the scaffold, as illustrated in Figure 5.7(d). Therefore, the positions

of the seeding cells are effectively controlled and optimized by the multiphysics model, it is thus confirmed that the present magnetic scaffold can provide a suitable cell mechanical microenvironment for tissue generation.

5.5.2. Biochemical response of the magnetic scaffold

It is commonly known that the biochemical cues such as growth factor, pH, and ion concentration, also play critical roles in biological systems [130, 277]. For example, the depletion of potassium (K^+) is associated with impaired carbohydrate and protein metabolism, neuromuscular and cardiac toxicity, and the abnormal renal function [278]. As such, the synergistic effects of the biophysical (e.g. mechanical stimulus) and biochemical cues are required to be fully considered in the design of bioreactor for providing appropriate culture condition [130]. Therefore, the concentration of the monovalent cation K^+ within the magnetic scaffold is predicted and optimized via the validated multiphysics model, when subjected to the varying material parameter such as initial fixed charge densities C_f^0 . Typically the concentration of K^+ ion is around 140 mM for regular cell growth medium [277, 279], herein the critical value is also adopted as the optimal concentration. In this study, the environmental solution contains the ions of K^+ , H^+ , Cl^- , and OH^- with pH of 7.4. The ion concentrations at the solution are $\bar{C}_{K^+} = \bar{C}_{Cl^-} = 120$ mM, the hydrogel-magnet distance $z_0 = 6$ mm, the current $I = 0.05$ A, and the remaining inputs are provided as section 5.5.1.

Figure 5.8. Influence of the initial fixed charge density C_f^0 on variation of the ion concentration C_{K^+} along the coordinate $R = 0$.

Figure 5.8 is plotted for influence of the initial fixed charge density C_f^0 on variation of the concentration C_{K^+} along the vertical line located at coordinate $R = 0$ across the domain over both the magnetic hydrogel and its surrounding solution. It is found that the initial fixed charge density C_f^0 has a pronounced impact on distribution of the concentration C_{K^+} . The concentration of K^+ ion remains almost unchanged in environmental solution, while a sharp increase or decrease is found at hydrogel-solution interface, and the concentration C_{K^+} inside the hydrogel is higher than that at the interior solution. Because the fixed charged groups merely exist in the anionic hydrogel and they attract numerous counterions from the environmental solution into the interior hydrogel for achieving the electroneutrality state. The phenomenon results in the imbalance of ionic concentration around the hydrogel-solution interface. As the valence of the fixed charge group is negative, the mobile ions with the same sign of the fixed charge groups are repelled from entering the interior hydrogel, while the mobile ions with the positive

sign (e.g. K^+) are attracted into the hydrogel. Therefore, the concentration of the K^+ ion is higher within the interior hydrogel than that in the exterior solution. It is also seen from the figure that, the concentration C_{K^+} reaches about 140 mM if the fixed charge density $C_f^0 = 38 \text{ mM}$. Therefore, the present magnetic scaffold enables to provide the desired biochemical cues, in addition to the biophysical cues such as mechanical stimulation, for the cell culture in tissue engineering by design and optimization of fixed charge groups within the hydrogel.

5.6. Remarks

In this work, the magnetic-pH-sensitive hydrogel-based scaffold has been investigated for optimization of cell biophysical and biochemical microenvironment, when subjected to the magnetic and pH coupled stimuli. In particular, the positions of seeding cells and the concentration of potassium (K^+) within the scaffold are optimized by a multi-effect-coupling magnetic-pH-stimuli (MECmpH) model based on threshold of the mechanical force for mechanotransduction effect at cellular-size level, and the requirement for the regular cell growth medium respectively. In the MECmpH model, the responsive mechanisms are considered, such as diffusions of solvent and ions, hydrogel magnetization, ionic polarization, and the nonlinear hydrogel deformation. To examine present MECmpH model, the simulation results are compared with the published experiment, for magnetic hydrogel under the pH and nonuniform magnetic effects respectively, where satisfactory agreements are achieved. Subsequently, the performance of the magnetic scaffold is studied in detail under different pH level and magnetic stimuli. The results show that higher pH level and magnetic intensity due to the current intensity,

and the shorter hydrogel-magnet distance contribute to the larger deformation of the magnetic scaffold and thus the stronger mechanical force acting on cells. Furthermore, the cell seeding position on the magnetic scaffold is optimized quantitatively by the multiphysics model. Apart from that, the physiological concentration of K^+ within the scaffold is also optimized by control of the initial fixed charge density of the scaffold. Therefore, the MECmpH model can well capture and predict the response of the dual magnetic-pH-sensitive hydrogel, and the presently optimized magnetic hydrogel-based scaffold may provide the right stimulatory conditions, such as biophysical and biochemical cues, resulting in efficient cell microenvironment *in vitro* and *in vivo*.

Chapter 6. Development of a Magneto-Mechanical Model for Magnetic Elastomer Microactuator

6.1. Introduction

This chapter extends the MECm model in Chapter 3 from solvent to air surrounding, in which a novel magneto-mechanical model is developed for characterization of the distributive magnetic field and the field-induced nonlinear deformation of the magnetic elastomer microactuator. In particular, the transition between the uniform and nonuniform magnetic fields is investigated, due to the reversible variation of the geometric size between the finite and infinite magnetic elastomers. This chapter is organized as follows. Following this section, Section 6.2 formulates the mathematical model with consideration of the Maxwell stress over the elastomer-surrounding interface, and the nonlinear magnetization in a proposed novel free energy density. The numerical implementation is described in Section 6.3, followed by model validation in Section 6.4. Subsequently, Section 6.5 analyzes the transition of the magnetic field from uniform to nonuniform magnetic fields, and vice versa subject to the geometrical variation of the magnetic elastomer. Furthermore, the critical point of the transition is determined and presented quantitatively by the magneto-mechanical model. Finally, several remarks are given in Section 6.6.

6.2. Formulation of the magneto-mechanical model

A novel magneto-mechanical model is developed in this section, with consideration of the Maxwell stress over the elastomer-surrounding interface and the nonlinear magnetization in a proposed novel free energy density.

6.2.1. Magnetic field

From Section 3.3.2, the Maxwell's equations for magnetic intensity $\mathbf{h}$ and $\mathbf{H}$, as well as magnetic induction $\mathbf{b}$ and $\mathbf{B}$ in Eulerian and Lagrangian coordinates are given respectively by

$$\nabla \times \mathbf{h} = 0, \quad \nabla \cdot \mathbf{b} = 0 \quad (6.1)$$

$$\nabla_{\mathbf{x}} \times \mathbf{H} = 0, \quad \nabla_{\mathbf{x}} \cdot \mathbf{B} = 0 \quad (6.2)$$

where $\nabla \times (\bullet)$ and $\nabla \cdot (\bullet)$ denote the spatial curl and divergence operators with respect to $\mathbf{x}$ respectively, and $\nabla_{\mathbf{x}} \times (\bullet)$ and $\nabla_{\mathbf{x}} \cdot (\bullet)$ the material curl and divergence operators with respect to $\mathbf{X}$. The transformation from the Eulerian description of the magnetic variables to the Lagrangian counterparts are given below

$$\mathbf{B} = \mathcal{J}\mathbf{F}^{-1}\mathbf{b}, \quad \mathbf{H} = \mathbf{F}^T\mathbf{h} \quad (6.3)$$

The corresponding magnetic boundary conditions are written as

$$\mathbf{N} \cdot [[\mathbf{B}]] = 0, \quad \mathbf{N} \times [[\mathbf{H}]] = 0 \quad (6.4)$$

where $\mathbf{N}$ is the unit outward normal to the surface boundary, and the double square bracket a quantity jump across the surface from the inside to outside of the material.

6.2.2. Mechanical field

In the absence of external force, the mechanical balance of the magnetic elastomer in the equilibrium state is written in the Lagrangian form of given by

$$\nabla_{\mathbf{x}} \cdot \mathbf{P} = 0 \quad (6.5)$$

where $\mathbf{P}$ denotes the nominal stress and related to the true stress $\boldsymbol{\sigma}$ by $\mathbf{P} = J\boldsymbol{\sigma}\mathbf{F}^{-T}$ [173].

At the elastomer-surrounding interface, the stress $\mathbf{P}$ satisfies the mechanical boundary condition below

$$\mathbf{P} \cdot \mathbf{N} = \mathbf{T}_m \quad (6.6)$$

where $\mathbf{T}_m$ is the magnetic traction acted on the exterior boundary and $\mathbf{T}_m = \mathbf{P}_m \cdot \mathbf{N}$, where the Lagrangian Maxwell stress $\mathbf{P}_m$ is defined as

$$\mathbf{P}_m = \mathbf{F}^{-T} (\mathbf{H} \otimes \mathbf{B}) - \frac{1}{2} (\mathbf{H} \cdot \mathbf{B}) \mathbf{F}^{-T} \quad (6.7)$$

6.2.3. Free energy density with nonlinear magnetization

For characterization of the behavior of the magnetic elastomer, the constitutive equations are required. From Equation (3.79), the stress $\mathbf{P}$ and magnetic induction $\mathbf{B}$ are respectively expressed as

$$\mathbf{P} = \frac{\partial \Omega}{\partial \mathbf{F}}, \quad \mathbf{B} = -\frac{\partial \Omega}{\partial \mathbf{H}} \quad (6.8)$$

where Ω is the total free energy per unit reference volume.

The present total free energy density Ω is contributed by the elasticity of the polymer networks Ω_{ela} and the magnetization Ω_{mag} . For finite but moderate deformation, a good approximation of the rubber elasticity may be represented by the neo-Hookean model [280]

$$\Omega_{ela} = \frac{G}{2} [\text{tr}(\mathbf{F}^T \mathbf{F}) - 3] \quad (6.9)$$

where G denotes the shear modulus of the magnetic elastomer.

If the magnetic elastomer exhibits paramagnetism and its magnetic induction $\mathbf{b}$ is linear with the applied magnetic intensity $\mathbf{h}$, the magnetization energy in current configuration is given by $\phi_{mag}(\mathbf{h}) = -\mu_{m0}(\mathbf{h} \cdot \mathbf{h})/2$ [281], where μ_{m0} is the initial magnetic permeability. By defining $\Omega_{mag}(\mathbf{F}, \mathbf{F}^T \mathbf{h}) = J\phi_{mag}(\mathbf{h})$ and considering nonlinear magnetization as well as the magnetic relation (6.3), the modified magnetization energy in reference configuration is proposed and presented by

$$\Omega_{mag} = -\frac{J}{2} [\boldsymbol{\mu}_m(\mathbf{F}^{-T} \mathbf{H}) \cdot (\mathbf{F}^{-T} \mathbf{H})] \quad (6.10)$$

where the diagonal tensor $\boldsymbol{\mu}_m$ denotes the magnetic permeability and is given by [282]

$$\mu_{mi} = \mu_0 [1 + m_s L(\zeta) / h_i] \quad (6.11)$$

where μ_{mi} and h_i are the magnitudes of the magnetic permeability and intensity along the i -axis respectively, $L(\zeta) = \coth(\zeta) - 1/\zeta$ the Langevin function and $\zeta = 3\chi_{m0}h_i/m_s$ (χ_{m0} is the initial magnetic susceptibility) [212], m_s the saturation magnetization of the magnetic elastomer that is associated with the volume fraction ξ_p and saturation magnetization m_{sat} of the magnetic particle via $m_s = \xi_p m_{sat}$ [283].

Based on Equations (6.9) and (6.10), and if the magnetic elastomer is assumed to be incompressible, namely $\det(\mathbf{F})=1$, the total free energy density Ω becomes

$$\Omega = \frac{G}{2}[\text{tr}(\mathbf{F}^T \mathbf{F}) - 3] - \frac{1}{2}[\boldsymbol{\mu}_m (\mathbf{F}^{-T} \mathbf{H}) \cdot (\mathbf{F}^{-T} \mathbf{H})] - p[\det(\mathbf{F}) - 1] \quad (6.12)$$

where p denotes the Lagrange multiplier.

By the free energy function (6.12) and the relation (6.8), the nominal stress $\mathbf{P}$ and magnetic induction $\mathbf{B}$ are rewritten respectively as

$$\mathbf{P} = G\mathbf{F} + \mathbf{F}^{-T} (\mathbf{H} \otimes \mathbf{H}) \mathbf{F}^{-1} (\boldsymbol{\mu}_m \mathbf{F}^{-T}) - p\mathbf{F}^{-T} \quad (6.13)$$

$$\mathbf{B} = \mathbf{F}^{-1} (\boldsymbol{\mu}_m \mathbf{F}^{-T}) \mathbf{H} \quad (6.14)$$

Alternatively, the above equations may also be rewritten in Eulerian form of

$$\boldsymbol{\sigma} = G\mathbf{F}\mathbf{F}^T + (\mathbf{h} \otimes \mathbf{h})\boldsymbol{\mu}_m - p\mathbf{I} \quad (6.15)$$

$$\mathbf{b} = \boldsymbol{\mu}_m \mathbf{h} \quad (6.16)$$

It is found that the first term on the right-hand side of Equation (6.15) is contributed from elasticity, and the second term denotes the Maxwell stress, where the hydrostatic part is absorbed in the hydrostatic pressure p .

Based on the Maxwell's equation (6.2), the magnetic intensity vector $\mathbf{H}$ is related to magnetic scalar potential ψ by $\mathbf{H} = -\nabla_{\mathbf{x}}\psi$. Substituting Equation (6.14) into (6.2), the

magnetic potential ψ in both the magnetic elastomer and its surrounding medium is formulated by the governing equation below

$$\nabla_{\mathbf{x}} \cdot [\mathbf{F}^{-1}(\boldsymbol{\mu}_m \mathbf{F}^{-T}) \nabla_{\mathbf{x}} \psi] = 0 \quad (6.17)$$

Combining Equations (6.1) and (6.16), the magnetic potential ψ also satisfies the following relation in current configuration

$$\nabla \cdot (\boldsymbol{\mu}_m \nabla \psi) = 0 \quad (6.18)$$

6.3. Numerical implementation

So far the model for the magnetic elastomer has been completed theoretically. In reference configuration, It consists of the magnetostatic equation (6.17) and mechanical balance equation (6.5). In addition, an explicit free energy density with consideration of nonlinear magnetization is included by Equation (6.12), and the constitutive relations by Equations (6.13) and (6.14). The corresponding magnetic and mechanical boundary conditions are presented via Equations (6.4) and (6.6).

For simplification of the numerical computation, a set of non-dimensional parameters is defined as follows

$$R^* = \frac{R}{L_R}, \mathbf{H}^* = \frac{\mathbf{H}}{H_0}, \mathbf{B}^* = \frac{\mathbf{B}}{\mu_0 H_0}, \psi^* = \frac{\psi}{L_R H_0}, p^* = \frac{p}{G}, \nabla_{\mathbf{x}}^* = L_R \nabla_{\mathbf{x}} \quad (6.19)$$

where L_R is the radial surrounding domain size, H_0 the magnitude of the applied magnetic intensity, and μ_0 the magnetic permeability of the vacuum.

By Equations (6.5), (6.13), and (6.17), the weak forms of the governing equations are rewritten as

$$\begin{aligned} & \int_{\Gamma_0} [\mathbf{F} + B_{0m} \mathbf{F}^{-T} (\mathbf{H}^* \otimes \mathbf{H}^*) \mathbf{F}^{-1} (\boldsymbol{\mu}_{mr} \mathbf{F}^{-T}) - p^* \mathbf{F}^{-T}] : \delta \mathbf{F} dV_0 \\ & = \int_{\Gamma_0} \mathbf{T}^* \cdot \delta \mathbf{x}^* dS_0 + \int_{\Gamma_0} \mathbf{F}_b^* \cdot \delta \mathbf{x}^* dV_0 \end{aligned} \quad (6.20)$$

$$\int_{\Gamma_0} [\mathbf{F}^{-1} (\boldsymbol{\mu}_{mr} \mathbf{F}^{-T}) \nabla_{\mathbf{x}}^* \psi^*] \cdot \nabla_{\mathbf{x}}^* (\delta \psi^*) dV_0 = \int_{\Gamma_0} B_{N^*}^* \cdot \delta \psi^* dS_0 \quad (6.21)$$

where Γ_0 is the computational domain covering the magnetic elastomer and its surrounding, $\boldsymbol{\mu}_{mr} = \boldsymbol{\mu}_m / \mu_0$ the relative magnetic permeability tensor, $B_{0m} = \mu_0 H_0^2 / G$ the magnetic bond number to denote the ratio of the magnetic to elastic contributions, $\mathbf{T}^* = \mathbf{P}^* \cdot \mathbf{N}^*$ and $B_{N^*}^* = \mathbf{B}^* \cdot \mathbf{N}^*$ the non-dimensional traction and magnetic induction along the unit normal $\mathbf{N}^*$ respectively.

The weak form of the incompressible constraint is given by [43]

$$\int_{\Gamma_0} [\det(\mathbf{F}) - 1] \delta p^* dV = 0 \quad (6.22)$$

The non-dimensional weak forms (6.20) to (6.22) constitute a magneto-mechanical system sufficient to determine the field evolution, and can be implemented directly in COMSOL Multiphysics 4.4 for the following analyses.

6.4. Validations of the model

In this section, two comparisons are made, (i) between the simulated magnetic field distribution and the analytical solution, and (ii) between the simulated elastomer deformation and the experimental result.

6.4.1. Distribution of the magnetic field

Usually the magnetic elastomer microactuator works in an infinite non-magnetic surrounding [284]. However, it is time-consuming to consider an infinite space when using a standard finite element method [184]. Alternatively, the optimized surrounding domain is obtained by study of the influences of the different surrounding sizes on performance of the magnetic elastomer.

Figure 6.1. Schematic of a spherical magnetic elastomer immersed in a non-magnetic surrounding medium under a uniform magnetic field.

In general, the analytical solution of the magnetic field distribution may only exist for either the magnetic elastomer of ellipsoidal shape or other shapes with infinite sizes

[150, 174]. Herein, a spherical magnetic elastomer is utilized for the distribution of the magnetic field, as shown in Figure 6.1. The elastomer with radius r_0 is centered in a non-magnetic surrounding of radius L_R and height. In the cylindrical coordinate with axial symmetry, only half of the computational domain is simulated. If the externally magnetic field imposed is weak, the elastomer is linearly magnetized and its magnetic permeability μ_m is rewritten as $\mu_{m0}\mathbf{I}$. For the axial symmetry problem, the Neumann magnetic boundary conditions are applied at the center of the magnetic elastomer to guarantee the continuity of the magnetic field, namely

$$\left. \frac{\partial \psi^*}{\partial R^*} \right|_{R^*=0} = 0 \quad (6.23)$$

and at the surrounding edge, the magnetic intensity $\mathbf{H}_0$ on the boundary ∂S_0 remains uniform or unperturbed, such that

$$\psi^*(R^*, 1) = 1, \psi^*(R^*, 0) = 0, \left. \frac{\partial \psi^*}{\partial R^*} \right|_{R^*=1} = 0 \quad (6.24)$$

At the elastomer-surrounding interface $\partial\beta_0$, the normal component of the magnetic induction and the tangential part of the magnetic intensity are continuous across the interface $\partial\beta_0$ according to the magnetic boundary condition (6.4), namely

$$[[\psi^*]] = 0, \mu_{m0} \left. \frac{\partial \psi^*}{\partial N^*} \right|_{\partial\beta_0^-} = \mu_0 \left. \frac{\partial \psi^*}{\partial N^*} \right|_{\partial\beta_0^+} \quad (6.25)$$

Based on the work of Afkhami *et al.* [285], the analytical solution of the magnetic field distribution for a spherical magnetic elastomer that placed in free space is computed by

$$\mathbf{H} = \begin{cases} A(\cos \theta \mathbf{e}_r - \sin \theta \mathbf{e}_\theta) & r \leq r_0 \\ (H_0 - 2D/r^3)\cos \theta \mathbf{e}_r - (H_0 + D/r^3)\sin \theta \mathbf{e}_\theta & r > r_0 \end{cases} \quad (6.26)$$

where θ is the polar angle, $A = \frac{3\mu_0}{\mu_{m0} + 2\mu_0} H_0$ and $D = -\frac{\mu_{m0} - \mu_0}{\mu_{m0} + 2\mu_0} r_0^3 H_0$.

Figure 6.2. Influence of the size of surrounding domain on the variation of non-dimensional axial magnetic field H_z^* along the non-dimensional coordinate $R^* = 0$.

For analysis of the influence of the surrounding size on the distribution of non-dimensional axial magnetic field H_z^* along the non-dimensional coordinate $R^* = 0$, Figure 6.2 is plotted to numerically compare the presently computed results with the theoretical counterparts, where $\mu_{m0} = 2\mu_0$ and $L_R = L_H$ [285]. To examine the predictive capability of the present model, the global error is calculated between the simulation and the analytical solution for the magnetic field distribution [269]. As observed from Figure

6.2, with the increase of the surrounding size L_R , the magnetic intensity H_Z^* gradually approximates the analytical solution. In particular, when L_R is eight times larger than the elastomer radius r_0 , the global error of less than 0.4% is found, as shown in Table 6.1. If L_R increases further from $8r_0$ to $10r_0$, no noticeable change is found in the global error from 0.4% to 0.39%. However, the number of computational elements increases significantly by about 50%. Therefore, the surrounding size $L_R = 8r_0$ is utilized for the subsequent analysis, with a consideration of the balance between the computational accuracy and cost.

Table 6.1. The influence of the surrounding size on the magnetic field distribution.

L_R	No. of elements	global error (%)
$2r_0$	3958	26.9
$4r_0$	7120	2.7
$6r_0$	15370	1.4
$8r_0$	27044	0.40
$10r_0$	41304	0.39

6.4.2. Equilibrium deformation of the magnetic elastomer

For further verification of the magneto-mechanical model, the presently predicted deformation of the magnetic elastomer in the equilibrium state is compared with the experimental data [77], where three types of cylindrical magnetic elastomers were synthesized by the silicon rubber and carbonyl iron particles with different volume fractions ξ_p , namely 15%, 20%, and 27% respectively. The elastomers were exposed to a uniform magnetic field ranging from 0 to 636 kA/m, and their magnetostrictive displacements were then recorded with increasing magnetic field, as shown in Figure 6.3.

The input parameters are given in Table 6.2, where the initial magnetic susceptibility χ_{m0} is estimated by the Maxwell-Garnett formula [286], and the shear modulus $G = G_0(1 + k_E \xi_p)$ due to the reinforcement of the filled magnetic particles [24] (here G_0 is the shear modulus of the unfilled elastomer and k_E the Einstein-Smallwood parameter).

Figure 6.3. Schematic of a cylindrical magnetic elastomer immersed in a non-magnetic surrounding subject to a uniform magnetic field.

Table 6.2. Input parameters for validation of the model of the magnetic elastomers.

parameter	symbol	value
initial radius of the elastomer	L_r	6 mm [77]
initial height of the elastomer	L_h	30 mm [77]
initial magnetic susceptibility	χ_{m0}	0.53, 0.75, 1.11 [286]
shear modulus	G	0.32, 0.35, 0.39 MPa [287] 1360 kA/m [288, 289] (used as input parameter for the validation)
saturation magnetization of the carbonyl iron particle	m_{sat}	840 kA/m [290], 1582 kA/m [291] (for information only)
Einstein-Smallwood parameter	k_E	2.5 [24]
external magnetic intensity	H_0	0 ~ 636 kA/m [77]

Figure 6.4 is illustrated to compare the simulated magnetostrictive displacement of the magnetic elastomer with the experimental counterpart [77]. As seen from the figure, a graduate increase in the magnetostriction is found with increasing magnetic intensity H_0 . Initially, it increases dramatically when the field H_0 is below 150 kA/m, while its increment decreases if H_0 increases from 150 to 500 kA/m. Afterwards, the minimal increase is found in the displacement with a further increasing H_0 . It is known that the deformation of the magnetic elastomer is determined by a balance between the magnetic and the elastic stresses, where the former is associated with the magnetization of the elastomer [243]. Based on the Langevin's theory of paramagnetism [285], the magnetization enlarges with the increasing magnetic field H_0 , whereas the increase rate drops gradually. When the magnetization reaches the elastomer saturation point, a further increase of the applied magnetic field is unable to enhance the magnetization, thus resulting in a saturated magnetostriction. It is also seen that, the deformation is significantly affected by the volume fraction of the magnetic particles ξ_p . Probably the higher magnetic particle concentration leads to a larger magnetic permeability that induces stronger magnetic force acting on the elastomer, and eventually drives the larger deformation [241, 292]. Furthermore, the figure also shows that the predicted deformation coincides with the experimental results quantitatively and qualitatively, where the global errors of 13.3%, 3.9%, and 3.7% are achieved for the three cylindrical elastomers with particle volume fractions ξ_p of 15%, 20%, and 27% respectively. As such, the validated model is capable of accurately characterizing the behavior of the magnetic elastomer, and then be used to undertake the studies described below.

Figure 6.4. Comparison of the magnetostrictive displacement between the simulation results and experimental data [77] for the magnetic elastomer with different particle volume fractions.

6.5. Analysis of magnetic field transition

For further understanding the actuation performance of the magnetic elastomer, it is vital to characterize the magnetic field distribution and field-induced nonlinear deformation. In general, magnetic elastomer may work with the geometric size ranging from the finite to infinite one for different actuation scenarios, which results in a magnetic field transition from the nonuniform to the uniform one, and vice versa. Herein, the magnetic-field transition behavior of the cylindrical magnetic elastomer is investigated when subjected to different aspect ratios. To the best of our knowledge, so far no effort has been done to study the transition phenomenon due to the geometric variation. Thereby, the validated magneto-mechanical model is first employed to investigate the transition qualitatively and quantitatively. The simulation is conducted with the following input data. The radius of the cylindrical magnetic elastomer $L_r = 10 \mu\text{m}$, the shear modulus $G = 100 \text{ kPa}$, the initial magnetic susceptibility $\chi_{m0} = 1$, the saturation magnetization $m_s = 100 \text{ kA/m}$, and

the geometric sizes, represented by aspect ratio $AR = L_h / L_r$, are 2, 4, 8, 16, and infinite respectively, as illustrated in Figure 6.3.

Figure 6.5 demonstrates influence of the aspect ratio AR on variation of the non-dimensional axial magnetic intensity H_z^* and magnetic induction B_z^* along a vertical line located at $R^* = 0$ across the cylindrical magnetic elastomer and its surrounding. As observed from Figure 6.5(a), the non-dimensional magnetic intensity H_z^* remains almost 1 when the normalized distance Z/L_H is less than 0.2, which demonstrates that the original uniform magnetic field remains unperturbed far away from the elastomer-surrounding interface. If the normalized distance Z/L_H increases continuously, the magnetic intensity H_z^* increases slightly and then drastically until it reaches the maximum near the interface. Subsequently, the magnetic intensity H_z^* follows a step function with a sharp decrease at the interface with a small range of the normalized distance Z/L_H , and it then rises up to another maximum. The figure also shows that the edge effect is more pronounced with decreasing aspect ratio AR . For example, when AR is 2, the magnetic intensity H_z^* approximates half of the maximum at the normalized distance 0.4, while it remains almost 1 when AR is 16. Furthermore, it is found that the magnetic intensity H_z^* within the magnetic elastomer is nonuniform, especially for the elastomer with AR of 2 or 4. If AR increases further, the uniformity of the magnetic field H_z^* increases, especially in the central part of the elastomer. As such, increasing the aspect ratio results in a more uniform magnetic field, and thus the magnetic field within the infinite elastomer is homogeneous and approximates the magnetic field applied prior

to insertion of the elastomer [293]. Such finding was mostly employed as an assumption to simplify the theoretical analysis, despite the fact that no experiment performed can satisfy the infinite size condition [47, 176]. In fact, the assumption may also be valid when the aspect ratio AR of the magnetic elastomer is sufficiently high to approximate the infinite condition with an accepted error [47], whereas the relevant quantitative analysis of the critical size for satisfying the assumption remains untouched, which will be discussed in Figure 6.8. As observed from Figure 6.5(b), the non-dimensional magnetic induction B_z^* is also greatly affected by the aspect ratio AR . When the ratio AR increases from 2 to 4, the maximum B_z^* within the magnetic elastomer increases by around 10%. However, the impact of AR on maximum B_z^* becomes less significant from 3.7% to 1.1% when it increases further from 4 to 8 or 8 to 16. Similarly to the distribution of H_z^* in Figure 6.5(a), the edge effect is more prominent for the magnetic elastomer with AR of 2 and 4, and the uniformity of B_z^* within the elastomer increases with increasing AR . However, different from the discontinuous distribution of H_z^* across the elastomer-surrounding interface, B_z^* is continuous through the interface to satisfy the magnetic boundary condition (6.4).

Figure 6.5. Influence of aspect ratio AR on variation of the distributions of non-dimensional (a) magnetic intensity H_z^* , and (b) magnetic induction B_z^* along the coordinate $R^* = 0$.

Figure 6.6 is plotted for analysis of the aspect ratio AR on variation of the non-dimensional axial magnetic intensity H_z^* and magnetic induction B_z^* along a horizontal line located at $Z/L_H = 0.5$ across the magnetic elastomer and its surrounding. Based on the magnetic boundary condition (6.4), the non-dimensional axial magnetic intensity H_z^* is tangential to the lateral interface, such that it goes across the interface continuously, as shown in Figure 6.6(a). It is also found that the uniformity of H_z^* within the magnetic elastomer increases gradually with increasing AR . When AR is 16, H_z^* approximates 1, which shows that the axial magnetic field within the elastomer is close to the surrounding field. In terms of the distribution of magnetic induction B_z^* , it jumps at the interface to satisfy the magnetic boundary condition (6.4), as shown in Figure 6.6(b).

Figure 6.6. Influence of aspect ratio AR on variation of the distributions of non-dimensional (a) magnetic intensity H_z^* , and (b) magnetic induction B_z^* along the coordinate $Z/L_H = 0.5$.

Figure 6.7 illustrates the two-dimensional (2D) distribution of the axial displacement w of the magnetic elastomer subject to different aspect ratios AR respectively, where $H_0 = 100$ kA/m. It is seen that the field-induced deformation is inhomogeneous across the magnetic elastomer, especially when the aspect ratio is 2 and 4, probably due to the inhomogeneous magnetic field distribution. However, it approaches homogeneous when AR increases from 4 to 8 or 16, especially for the central part of the elastomer, which is similar to the magnetic field distribution. Therefore, the homogeneous deformation is expected if the aspect ratio is large enough.

Figure 6.7. 2D distribution of the axial displacement w with different aspect ratios: (a) $AR=2$; (b) $AR=4$; (c) $AR=8$; (d) $AR=16$.

For analysis of the transition between the uniform and nonuniform magnetic fields due to the geometric variation quantitatively, Figure 6.8 exemplifies the change of the non-dimensional average axial magnetic intensity $\langle H_z^* \rangle$ within the magnetic elastomer against the aspect ratio AR . The average magnetic intensity $\langle H_z^* \rangle$ increases monotonically with the continuous increase of AR from 2 to 16. Based on the work of Dalrymple *et al.* [47], if the difference of the magnetic field between the internal

elastomer and externally applied magnetic field is less than 5%, the geometric size of the elastomer can be regarded as infinite. As observed from Figure 6.8, the average magnetic field $\langle H_z^* \rangle$ is 0.95 when AR is 12.4. Therefore, the present cylindrical magnetic elastomer undergoes a transition from the nonuniform to uniform magnetic fields, if it reaches the critical point $AR = 12.4$. The finding is of potential interest for both the experimental and theoretical works on characterization of the magnetic elastomer. For example, if the geometric size of the magnetic elastomer in an experiment is in finite range with AR lower than the critical point, the model developed is required to consider the influences of the surrounding and interface, due to the nonuniform magnetic field distribution. Conversely, if an elastomer is employed experimentally with AR higher than the critical value, the model can be simplified by neglecting influences of the surrounding and interface.

Figure 6.8. Variation of non-dimensional average magnetic field $\langle H_z^* \rangle$ against the aspect ratio AR .

6.6. **Remarks**

To improve and optimize the actuation performance of the magnetic elastomer microactuator, the magnetic field distribution and the nonlinear deformation are investigated by a magneto-mechanical model. In particular, the transition from the nonuniform to uniform magnetic field, and vice versa, due to the geometric variation of the magnetic elastomers from the finite to infinite sizes. In this work, the influences of the surrounding, the Maxwell stress over the elastomer-surrounding interface, and the nonlinear magnetization are considered. The developed model is validated with both the experimental result and the analytical solution, and good agreements between them are achieved. It is then found that the increase of the geometric size of the magnetic elastomer contributes to the uniformity of both the magnetic field and the field-induced nonlinear deformation. Furthermore, it suggests that when the aspect ratio of the present cylindrical magnetic elastomer increases to a critical point, such as 12.4, it undergoes the transition. The finding is useful for both the experimental and theoretical works on characterization of the magnetic elastomer as microactuator in MEMS devices.

Chapter 7. Conclusions and Recommendations

7.1. Conclusions from the present work

The present research work deals with the development of the robust multiphysics models for magnetic hydrogels and elastomers subject to various magnetic and/or other coupled stimuli, which are validated with experimental and theoretical results in open literature, and solved numerically by the commercial finite element solver, COMSOL Multiphysics. The multiphysics models provide detailed descriptions of the magnetization, transports of solvent and ionic species, ionic polarization, and nonlinear mechanical behaviors in magnetic hydrogels, as well as the magneto-mechanical behavior with nonlinear magnetization in magnetic elastomers. Furthermore, they are successfully employed for design and optimization of the material properties, and the magnetic hydrogel- and elastomer- based devices. Therefore, the following four main achievements are achieved in this thesis.

The first achievement of the present work is development of a multi-effect-coupling magnetic-stimulus (MECm) model for the magnetic-sensitive hydrogel, with the effects of magneto-chemo-mechanical coupled fields.

- In this MECm model, the magnetic susceptibility for magnetization of the general magnetic hydrogel is defined as a function of finite deformation, instead of a constant for an ideal magnetic hydrogel. The constitutive equations, achieved by the second law of thermodynamics, consider the effects of the chemical potential, the externally applied magnetic field, and the finite deformation. In addition, the novel

free energy density is proposed with the magnetic effect associated with finite deformation, instead of volume fraction.

- The MECm model is validated through comparison between the simulated results and the experimental finding for deformation of the magnetic hydrogel in the equilibrium state, where satisfactory agreements are achieved.
- The parameter studies for optimized design of the magnetic hydrogel are carried out for influences of the magnetic and geometric properties, including the magnetic intensity, shear modulus, and volume fraction of the magnetic particles, on the behavior of the magnetic hydrogel in the equilibrium state. It is found that the swelling behavior of the magnetic hydrogel is much dependent on the external uniform magnetic field, where the volume swelling ratio decreases when the magnetic induction increases. Under a nonuniform magnetic field, the instability at the long-time scale starts at a lower current and the width of hysteresis is much smaller than that at short-time scale, and the stretch is larger at long-time scale than that at short-time scale. Furthermore, the initial swelling ratio without magnetic effect increases with the decrease of the particle volume fraction.

The second achievement is the extension of the MECm model for characterization of the transient fluid-structure interaction of the deformable magnetic hydrogel with surrounding fluid flow, through the fully coupled arbitrary Lagrangian-Eulerian (ALE) algorithm. The extended model is validated by comparing with both the finite difference solution and published experimental result, where good coincidence between them is attained. It is verified that the present model enables to predict the transient performance

of the magnetic hydrogel. Furthermore, two magnetic hydrogel-based devices are designed and optimized by the extended multiphysics model.

- The first is the magnetic-sensitive hydrogel-based microfluidic system for replicating various physiological and pathological conditions in the human body, by which the desired flow patterns can be generated in real time due to the fast-response deformation of the magnetic hydrogel. In the present work, the transient behavior of the magnetic hydrogel is investigated in detail, it is found that the response time for the magnetic hydrogel is improved significantly by 78% in a uniform magnetic field of 300kA/m, compared with that in the free swelling hydrogel without the magnetic effect. Furthermore, various patterns of pulsatile flow are generated for mimicking cell physiological microenvironment experienced by the bone marrow stromal cells, and also for the pathological condition at the femoral artery during diastole and systole, respectively
- The second device is the magnetic-sensitive hydrogel-based drug targeting system for delivering the movable and deformable drug-loaded hydrogel to the specific site. The results show that the higher flow velocity and/or the larger hydrogel size accelerate the movement of the hydrogel, while the smaller hydrogel size contributes to the larger swelling ratio. Furthermore, the performance of the magnetic targeting system is optimized for delivering the drug-loaded hydrogel to the specific site by tuning the maximum magnetic field strength and the magnet position.

The third achievement is the development of a multi-effect-coupling magnetic-pH-stimuli (MECmpH) model for optimization of cell physiological microenvironment

within the magnetic-pH-sensitive hydrogel-based scaffold. In particular, the positions of seeding cells and the concentration of potassium (K^+) within the scaffold are optimized by a multi-effect-coupling magnetic-pH-stimuli (MECmpH) model.

- In the MECmpH model, the four responsive mechanisms of the magnetic hydrogel are characterized, including hydrogel magnetization, ionic polarization, diffusions of the solvent and ions, and nonlinear finite deformation, when subjected to various biophysical and biochemical stimuli, such as the magnetic field due to current intensity and the solution pH.
- After validation of the MECmpH model with experimental result in open literature, it is found that the higher pH level and current intensity, and the shorter hydrogel-magnet distance contribute to the larger deformation of the magnetic scaffold and thus the stronger mechanical force on cells. Moreover, the cell seeding positions within magnetic scaffold are optimized for better cell culture through the controllable current intensity. Furthermore, the physiological concentration of K^+ within the scaffold is also optimized by the initial fixed charge density of the scaffold.

The last achievement is the development of a magneto-mechanical model for magnetic elastomer microactuator, where the transition is investigated between the uniform and nonuniform magnetic fields and the field-induced nonlinear deformation, due to reversible variation of the geometric size of the magnetic elastomer from infinite to finite one. In this study, both the elastomer and its surrounding medium are covered in the computational domain, where the Maxwell stress over the elastomer-surrounding interface is considered as an additional mechanical boundary, and the nonlinear

magnetization included in a proposed free energy density. After verification of the present model with both theoretical and experimental works, it is concluded that increasing the geometric size of the magnetic elastomer leads to a more uniform magnetic field, and thus the elastomer undergoes the transition from the nonuniform to uniform magnetic fields, if its size increases to a critical point.

In conclusion, the entire thesis is constituted by the four contributions mentioned above. It is believed that the present work is significant to understand the fundamental mechanism of the magnetic hydrogels and elastomers, and contributes to the design and optimization of the magnetic hydrogel- and elastomer-based devices in bioengineering and BioMEMS.

7.2. Recommendations for the future work

On the basis of the research works completed in this thesis, several potential topics associated with the multiphysics modeling of magnetic hydrogels and elastomers are recommended below for future works.

- It would be interesting to improve the constitutive equations in the present MECm and MECmpH models for the magnetic-sensitive and magnetic-pH-sensitive hydrogels respectively, by considering more effects on the constitutive relations. For example, the pore size of the hydrogel may have a significant impact on diffusions of solvent and ions, where the larger pore size may result in the faster diffusion rate. The environment temperature may be another physical factor to be considered on diffusions of the solvent and ions, and the interaction of the mobile ions with the fixed charge. The viscoelasticity is also required to be considered if a

local mechanical property of a gel is characterized at length scale below micrometers, such as nano-indentation. In this case, the short length for solvent migration reduces the swelling time to a value comparable to the characteristic time of viscoelasticity, and the deformation appears to be dominantly viscoelastic.

- The MECmpH model has been developed to quantitatively predict the responsive behavior of the dual magnetic-pH-sensitive hydrogel at steady state. However, a lot of biomedical applications request deep understanding of the kinetics of hydrogel behavior such as the pulsatile drug release. In addition, the relationship between the transient performance and the external stimuli is necessarily investigated for a comprehensive understanding of the fundamental mechanism of the environmental-sensitive hydrogel. As such, it is recommended to simulate and analyze the transient behavior of the hydrogel under various biochemical and biophysical stimuli.
- The macroscopic magneto-mechanical model has been formulated to characterize the magnetic field distribution and the field-induced nonlinear deformation of the magnetic elastomer. However, the microstructures, such as particle size and its arrangement may play a significant role in the overall macroscopic deformation and the mechanical property of the magnetic elastomer. Therefore, it is definitely worthwhile to formulate a novel microstructure-based magneto-mechanical model by incorporation of more microscopic information.
- The present work has theoretically developed multiphysics models for magnetic hydrogels and elastomers. The developed models can predict the performances of the hydrogels and elastomers that are not observed in the current experiments, such as magnetic-induced instability coupled with hysteresis and the magnetic field

transition associated with geometry. Therefore, it is definitely a worthwhile work to conduct experiments under the guide of the present numerical simulations

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Publications arising from the thesis

Journal Papers

1. **Q. Liu**, H. Li, K.Y. Lam, Development of a multiphysics model to characterize the responsive behavior of magnetic-sensitive hydrogels with finite deformation, *ACS J. Phys. Chem. B* 121(22) (2017) 5633-5646.
2. **Q. Liu**, H. Li, K.Y. Lam, Model development and numerical simulation of magnetic-sensitive hydrogels subject to an externally applied magnetic field, *Procedia Eng.* 214 (2017) 93-97.
3. **Q. Liu**, H. Li, K.Y. Lam, Transition of magnetic field due to geometry of magneto-active elastomer microactuator with nonlinear deformation, *IEEE/ASME J. Microelectromech. Syst.* 27(2) (2018) 127-136.
4. **Q. Liu**, H. Li, K.Y. Lam, Optimization of deformable magnetic-sensitive hydrogel-based targeting system in suspension fluid for site-specific drug delivery, *ACS Mol. Pharmaceutics* 15(10) (2018) 4632-4642.
5. **Q. Liu**, H. Li, K.Y. Lam, Modeling of a fast-response magnetic-sensitive hydrogel for dynamic control of microfluidic flow, *Phys. Chem. Chem. Phys.* 21 (2019) 1852-1862.
6. **Q. Liu**, H. Li, K.Y. Lam, Optimization of cell microenvironment of dual magnetic-pH-sensitive hydrogel-based scaffold. (Under Review).
7. **Q. Liu**, M. Liu, H. Li, K.Y. Lam, Multiphysics modeling of responsive deformation of dual magnetic-pH-sensitive hydrogel subject to magneto-chemo-electro-mechanical coupled field. (Under review)

Conference Papers

1. **Q. Liu**, H. Li, K.Y. Lam, Modeling and simulation of magnetic-sensitive elastomer immersed in surrounding medium. 10th European Conference on Constitutive Models for Rubbers (ECCMR2017), August 2017, Munich, Germany. (Oral Presentation)
2. **Q. Liu**, H. Li, K.Y. Lam, Model development and numerical simulation of magnetic-sensitive hydrogels subject to an externally applied magnetic field. 9th International Conference on Materials for Advanced Technologies (ICMAT2017), June 2017, Singapore. (Oral Presentation)