

A STUDY OF FERROMAGNETIC MICRO-ROD CLUSTER DYNAMICS UNDER
MAGNETIC FIELDS AND ITS APPLICATIONS IN STROKE TREATMENT

by

RUI CHENG

(Under the Directions of Yiping Zhao and Leidong Mao)

ABSTRACT

Dynamic control and structural manipulation of magnetic micro- clusters in a suspension are essential for their applications in stroke treatment, fluidic actuators and smart materials. Due to their anisotropic shape and magnetism, ferromagnetic micro-rod clusters (FMRCs) exhibit unique behaviors under both static and dynamic magnetic fields. The results are summarized here: (1) A rotation-extension coupled motion of FMRCs can be triggered by a static magnetic field, which results in a rearrangement of FMRCs; (2) A structural transition of FMRCs from stripy patterns to cellular network can be controlled by a transverse magnetic field; (3) Molecular diffusivity can be enhanced by rotating FMRCs, which eventually accelerates diffusion-limited thrombolysis and reduces risks of stroke treatment.

INDEX WORDS: Ferromagnetic micro- rods, Clustering, Dynamic behavior, Structural Transition, Thrombolysis, Stroke treatment.

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A Dissertation Submitted to the Graduate Faculty of the University of Georgia in Partial
Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

ATHENS, GEORGIA

2016

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ACKNOWLEDGEMENTS

I would like to thank my advisors Dr. Leidong Mao and Dr. Yiping Zhao for their academic guidance, scientific insight and financial support, without whom this dissertation would not have been possible.

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CHAPTER 1

INTRODUCTION

1.1 Magnetic and Hydrodynamic Effects on Single Particles

Micro- /nano- particles manipulated by an external magnetic field at low Reynolds number fluid has attracted attentions for their wide applications in science and engineering, such as in microfluidic sensors and actuators, biomedical detection and diagnostics, drug delivery and hyperthermia, and high throughput materials preparation. Such micro- /nano- magnetic motors are designed and fabricated in beads, rods, wires, helixes, even in assembled structures. Compared to catalytically powered nanomotors, the magnetic ones take advantages in fuel-free propulsion, wireless control and robust guidance. Based on their materials, sizes and shapes, the motors exhibit different magnetic properties and dynamic behaviors, and require different manipulating principles.

All materials fall into the three categories based on their magnetic response to an applied magnetic field, including diamagnetism, paramagnetism, and ferromagnetism. When the material is magnetized by a weak magnetic field, its magnetization $\vec{M}$ has a linear relationship with $\vec{H}$

$$\vec{M} = \chi \vec{H}, \quad (1.1)$$

where χ is a dimensionless number called magnetic susceptibility. Diamagnetic materials have no net atomic or molecular magnetic moment¹ and do not exhibit magnetic interaction when subjected to an external magnetic field. Thus, the magnetic susceptibility χ is

negative or equal to zero. In contrast, both paramagnetic and ferromagnetic materials can be magnetized due to the alignment of their intrinsic net magnetic moment with the applied field. Therefore, the magnetic susceptibilities χ of both materials are larger than zero, while ferromagnetic materials normally have a larger χ than that of paramagnetic materials. Ferromagnetic materials also have strong remanent magnetization, while paramagnetic materials have no apparent magnetization when the external field is not present.

Magnetic force $\vec{F}_m$ and magnetic torques $\vec{\Gamma}_m$ are present on a single magnetic particle under an external magnetic field $\vec{H}$. A general expression for the force $\vec{F}_m$ on a magnetized particle in a liquid under a magnetic field $\vec{H}$ is shown in Eq. (1.2)²

$$\vec{F}_m = \mu_0 V \left[(\vec{M}_p - \vec{M}_f) \cdot \nabla \right] \vec{H}, \quad (1.2)$$

where $\mu_0 = 4\pi \times 10^{-7} \text{ H m}^{-1}$ is the permeability of free space, V is the volume of the magnetized body, $\vec{M}_p$ is its magnetization, $\vec{M}_f$ is magnetization of the liquid surrounding the body, and $\vec{H}$ is magnetic field strength at the center of the body. When the particle and the carrier fluid under weak magnetic fields, according to Eq. (1.1), magnetizations of both the body $\vec{M}_p$ and the liquid magnetism $\vec{M}_f$ depend approximately linearly on the applied field, resulting in $\vec{M}_p = c_p \vec{H}$ and $\vec{M}_f = c_f \vec{H}$, where c_p and c_f are the dimensionless volume magnetic susceptibilities of the particle and the fluid. The magnetic force takes the form of Eq. (1.2), which is often cited in the literature as³⁻⁵

$$\vec{F} = \frac{V(\chi_p - \chi_f)}{\mu_0} (\vec{B} \cdot \nabla) \vec{B}, \quad (1.3)$$

where $\vec{B}$ is magnetic flux density. For particles manipulation in the carrier fluids under strong magnetic fields, Equation (1.3) is no longer valid as the magnetization of a particle and a carrier fluid may depend nonlinearly on the applied field or already reach to their saturated values. In this case, the magnetization process of both the particle and fluid can be modeled accurately by the classical Langevin theory. Langevin theory considers magnetic nanoparticles in a superparamagnetic bead and a fluid as a collection of monodispersed and non-interacting magnetic dipoles.² This approach leads to the Langevin function of magnetization² in Eq. (1.4)

$$\begin{aligned} \frac{\vec{M}_p}{\phi_p \vec{M}_{p,b}} &= L(\alpha_p) = \coth(\alpha_p) - \frac{1}{\alpha_p} \\ \frac{\vec{M}_f}{\phi_f \vec{M}_{f,b}} &= L(\alpha_f) = \coth(\alpha_f) - \frac{1}{\alpha_f} \end{aligned} \quad (1.4)$$

where $a_p = \mu_0 \rho M_{p,b} H d_p^3 / 6 k_B T$ and $a_f = \mu_0 \rho M_{f,b} H d_f^3 / 6 k_B T$. f_p and f_f are volume fractions of the magnetic materials, $M_{p,b}$ and $M_{f,b}$ are saturation magnetic moments of the bulk magnetic materials, and d_p and d_f are diameters of nanoparticles embedded in a magnetic micro particle and a fluid, respectively. k_B is the Boltzmann constant and T is the temperature.

When a B field is applied, paramagnetic particles are magnetized in the same direction of the field. However, magnetization exists in a ferromagnetic particle even before a is applied. As a result, there is a magnetic torque $\vec{\Gamma}_m$ induced by the B field due to the angle between $\vec{M}$ and $\vec{B}$

$$\vec{\Gamma}_m = \vec{m} \times \vec{B}, \vec{m} = V \vec{M} \quad (1.5)$$

where V and $\vec{m}$ is the volume and the magnetic moment of the particle. The torque rotates the particle until its magnetization aligns with $\vec{B}$.

The focus of this dissertation is to study ferromagnetic rods and clusters in low Reynolds number fluids. As a result, hydrodynamic force $\vec{F}_h$ and torque $\vec{\Gamma}_h$ are as important as magnetic ones. Based on Stokes' equation, the hydrodynamic force and torque on a spherical particle in a laminar flow is⁶

$$\begin{aligned}\vec{F}_h &= -3\pi\eta D_p (\vec{U}_p - \vec{U}_f), \\ \vec{\Gamma}_h &= -\pi\eta D_p^3 \vec{\Omega}\end{aligned}\tag{1.6}$$

where D_p is the diameter of the particle, $\vec{U}_p$ and $\vec{U}_f$ are the translational velocity of the particle and the fluid, and $\vec{\Omega}$ is the angular velocity of the particle.

In the case of a cylindrical rod with length l , diameter d and aspect ratio $\gamma = l/d$, the hydrodynamic force depends on the aspect ratio of the rod, and the angle between rod axes and its moving direction. When a rod moves at a relative velocity $\vec{U} = \vec{U}_p - \vec{U}_f$ in a Stokes' flow, the hydrodynamic forces induced by the axial flow, $\vec{F}_{h_{\parallel}}$, and the transverse flow, $\vec{F}_{h_{\perp}}$, can be expressed as

$$\vec{F}_{h_{\parallel}} = -\varepsilon_{\parallel} l \vec{U}, \vec{F}_{h_{\perp}} = -\varepsilon_{\perp} l \vec{U},\tag{1.7}$$

where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the axial and transverse drag coefficient per unit length, of which expression are summarized in Tab. 1.1.

Table 1.1 The hydrodynamic drag coefficient per unit length on a slender particle induced by an axial flow and a transverse flow of velocity $\vec{U}$.

	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$
--	---------------------------	-----------------------

<i>Hancock's results</i> ⁷	$\frac{2\pi\eta}{\ln(2\gamma)}$	$\frac{4\pi\eta}{\ln(2\gamma)}$
<i>Chwang's results</i> ⁸	$\frac{2\pi\eta}{\ln(2\gamma)-0.5}$	$\frac{4\pi\eta}{\ln(2\gamma)+0.5}$
<i>Tillett's results</i> ⁹	$\frac{2\pi\eta}{\ln(2\gamma)-0.5} + o\left(\frac{1}{\gamma^2} \ln \frac{1}{\gamma}\right)\eta$	$\frac{4\pi\eta}{\ln(2\gamma)+0.5} + o\left(\frac{1}{\gamma^2} \ln \frac{1}{\gamma}\right)\eta$
<i>Cox's results</i> ¹⁰	$\frac{2\pi\eta}{\ln(2\gamma)-0.81} + o\left(0.5\eta(\ln \gamma)^{-3}\right)$	$\frac{4\pi\eta}{\ln(2\gamma)+0.19} + o\left(0.5\eta(\ln \gamma)^{-3}\right)$

When the aspect ratio is small, the ratio of the hydrodynamic drag in the axial direction and in the transverse direction is about 1,¹¹⁻¹² i.e., $\varepsilon_{\parallel} = \varepsilon_{\perp} = \varepsilon$. Then, the hydrodynamic torque $\vec{\Gamma}_h$ on a rotating rod with an angular velocity of $\vec{\Omega}$ can be expressed as

$$\vec{\Gamma}_h = -2 \int_{x=0}^a \varepsilon_{\perp} \vec{\Omega} x^2 dx = -\frac{2}{3} \varepsilon_{\perp} \vec{\Omega} a^3. \quad (1.8)$$

The hydrodynamic drag is the primary resistance for the translational motion of the particle driven by the magnetic force. However, there is another kind of micro-swimmers in nature persistently harvest thrust energy from the resistance of surrounding fluids without losing external potentials. These micro-swimmers, such as prokaryotic and eukaryotic micro-organisms,¹³⁻¹⁵ achieve the locomotion with the movement of its flagella or cilia, of which mechanical principle is known as “drag-based thrust”.¹³ The drag-based thrust is caused by the anisotropic hydrodynamic interaction between the solid body and the carrier liquid, so that the net force of the hydrodynamic drag on the micro-swimmer plays as the propulsion force in the direction of the locomotion. The hydrodynamic interaction, including the hydrodynamic drag force $\vec{F}_h$ and torque $\vec{\Gamma}_h$, of a solid body

submerged in a viscous liquid can be related to its locomotion with a “resistance” matrix M_h ¹³

$$\begin{bmatrix} \vec{F}_h \\ \vec{\Gamma}_h \end{bmatrix} = M_h \begin{bmatrix} \vec{U} \\ \vec{\Omega} \end{bmatrix}, M_h = \begin{bmatrix} a & b \\ b^T & c \end{bmatrix}, \quad (1.9)$$

where a , b and c are the hydrodynamic drag coefficients of M_h and the resistant matrix M_h has to be symmetric according to the reciprocal theorem of Stokes flow.¹⁶

1.2 Magnetic Clustering under a Static Magnetic Field

For ferromagnetic particles (FMPs), even without an external B field, they naturally aggregate to form worm-like clusters due to their remnant magnetization and interactions.¹⁷⁻¹⁹ When a B field is applied, the clusters tend to uncurl and align in the B field direction due to the magnetic interaction between the particles and the external B field.^{17, 19}

To study the aggregation of ferromagnetic particles, we consider the magnetic energy of two dipole system, which incorporates both dipole-dipole interaction and dipole-field interaction. Figure 1.1 shows two magnetic dipoles $\vec{m}_1$ and $\vec{m}_2$ separated by $\vec{r}$. Magnetic energy E_m due to the interaction of the two magnetic dipoles is given as²⁰

$$E_m = -\frac{\mu_0 m_1 m_2}{4\pi r^3} \left[\frac{1}{2} \cos(\theta_1 - \theta_2) + \frac{3}{2} \cos(\theta_1 + \theta_2 - 2\theta_3) \right], \quad (1.10)$$

where m_1 and m_2 is the magnetic moment of the dipoles with angles of θ_1 and θ_2 , r is the center-to-center distance with an angle θ_3 . The magnetic force has two components, one is along the radial direction F_r , and the other is along tangential direction F_θ

$$F_r = -\frac{\partial E_m}{\partial r} = -\frac{3\mu_0 m_1 m_2}{4\pi r^4} \left[\frac{1}{2} \cos(\theta_1 - \theta_2) + \frac{3}{2} \cos(\theta_1 + \theta_2 - 2\theta_3) \right] \quad (1.11)$$

$$F_\theta = -\frac{\partial E_m}{r \partial (\theta_3)} = \frac{3\mu_0 m_1 m_2}{4\pi r^4} \sin(\theta_1 + \theta_2 - 2\theta_3)$$

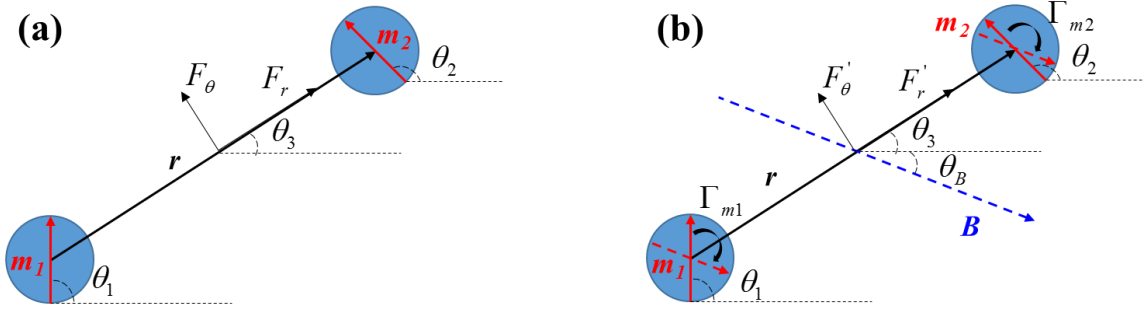


Figure 1.1 The magnetic interaction between two magnetic dipoles (a) without B field and (b) with a uniform B field.

When a uniform external B field is applied as shown in Fig. 1.1(b), there is an additional magnetic energy E_B induced between the moments $\vec{m}_1$ (and $\vec{m}_2$) and $\vec{B}$

$$E_B = \sum_{k=1}^2 m_k B (1 - \cos(\theta_B - \theta_k)), \quad (1.12)$$

where B and θ_B is the magnitude and orientation of the B field with respect to the horizontal direction. This energy decreases to 0 when both the $\vec{m}_1$ and $\vec{m}_2$ align with $\vec{B}$. By considering both Eqs. (1.10) and (1.12), the total energy E_t of magnetic interaction is

$$E_t = E_m + E_B. \quad (1.13)$$

When magnetic moments $\vec{m}_1$ and $\vec{m}_2$ are aligned with $\vec{B}$ ($\theta_1 = \theta_2 = \theta_B$), we have the magnetic force components F_r' and F_θ'

$$F_r' = -\frac{3\mu_0 m_1 m_2}{4\pi r^4} [3\cos^2(\theta_B - \theta_3) - 1]$$

$$F_\theta' = \frac{3\mu_0 m_1 m_2}{2\pi r^4} \sin(\theta_B - \theta_3) \cos(\theta_B - \theta_3) \quad (1.14)$$

Obviously, the aggregation is a transient assembly of magnetic particles while the chain length $L(t)$ is a function of time t . Combining the Smoluchowski equation and the diffusion-limited aggregation, the transient chain length $L(t)$ is found to follow a power law with respect to time t ²¹⁻²⁴

$$L(t) \propto \left(\frac{t}{t_B} \right)^Z, t_B = \frac{a^2}{24 \left[\left(\frac{1}{3} \right)^{0.5} - \left(\frac{1}{3} \right)^{1.5} \right] \sigma \Phi D}, \quad (1.15)$$

where Z is the dynamic exponent varies from 0.3 to 1, t_B is the characteristic time scale, a and Φ is the average radius and the volume fraction of the particles in the suspension. D is the thermal diffusivity of the magnetic particle, which can be estimated by Einstein's equation, $D = \frac{\kappa_B T}{6\pi\eta a}$, where T is the temperature and κ_B is the Boltzmann constant.

$\sigma = \frac{\mu_0 m^2}{16\pi a^3 \kappa T}$, is a dimensionless number for the ratio of magnetic energy to the thermal energy.

In this dissertation, we focus on the clustering behavior of ferromagnetic rods (FMR) under an external B field. Clustering of ferromagnetic rods (FMRs) is much more complicated compared to that of spherical particles. Though some efforts have focused on their unique properties and applications,²⁵⁻²⁸ ferromagnetic rod clusters (FMRCs) is not well understood to the best of our knowledge. Aoshima and Satoh conducted a two-dimensional (2D) Monte Carlo simulation on the clustering of FMRs without an external B -field.²⁹ As shown in Fig. 1.2 (a), they found that FMR aggregations consisted of a few fundamental structures, including anti-parallel particle pairs, raft-like clusters, and triangle-loop-like clusters.

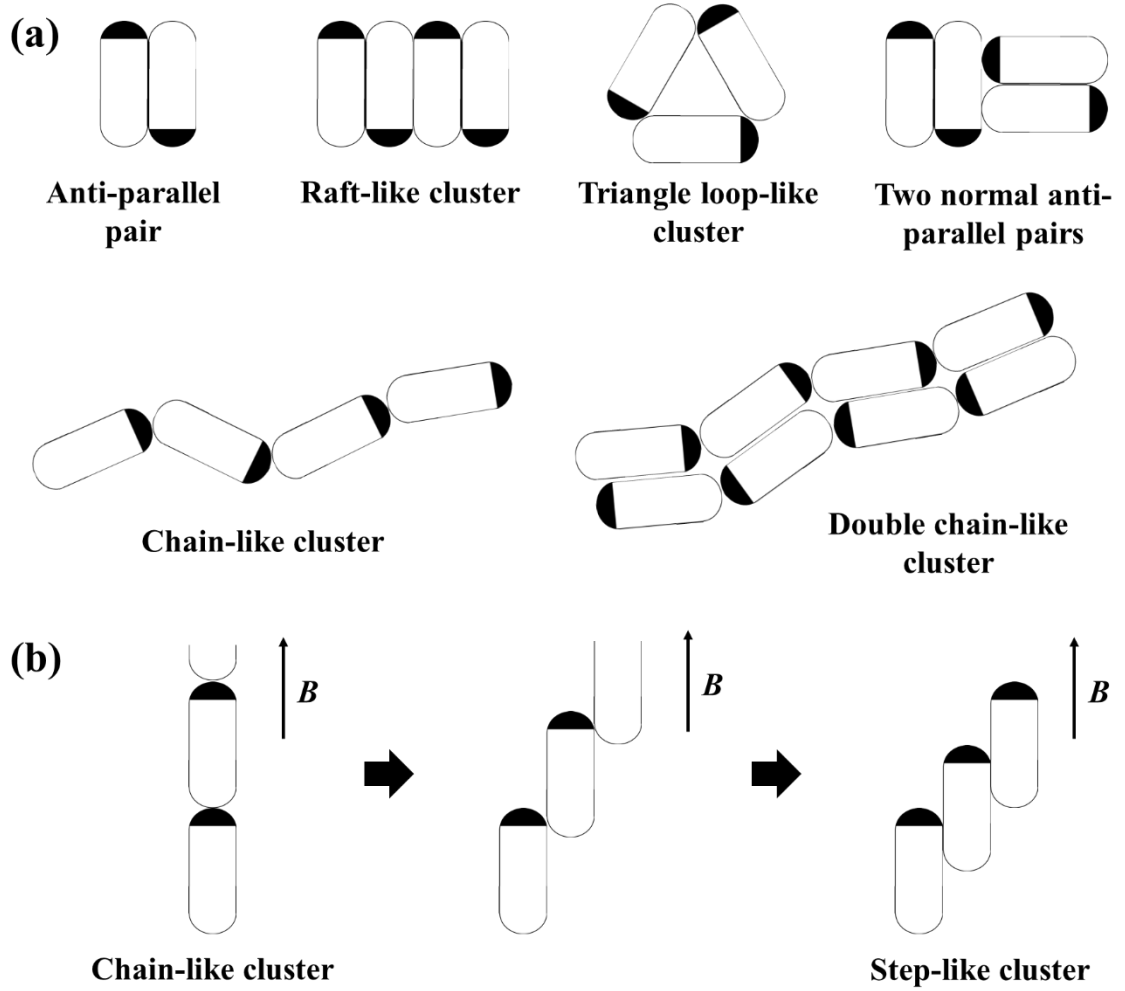


Figure 1.2 The fundamental structure of FMRs (a) with the absence of a B -field,²⁹ and (b) with the presence of a B -field.¹⁹

Particularly, the raft-like cluster is more stable than other structures when the aspect ratio of FMRs is larger than 2, which was experimentally obtained with Nickel nanorods.³⁰⁻
³¹ They also investigated the influence of an external B -field on the rod clustering *via* a 2D Monte Carlo simulation.¹⁹ It was found that adjacent FMRs aligned end-to-end along the field direction, forming two types of joints, a step-like structure in high concentration suspension, and a chain-like structure in low concentration suspension, as shown in Fig. 1.2(b).

1.3 Magnetic Clustering under a Dynamic Magnetic Field

A dynamic magnetic field has time-dependent changes either on its magnitude or its direction. As a result, complex structures are expected to form within a dynamic magnetic field. One of such complex structures is the chain growth. Shape and size of 1D magnetic chain of paramagnetic beads under a rotational magnetic field was studied theoretically and experimentally.³²⁻³⁵ Chain length is determined by the competition of magnetic torque and hydrodynamic torque. A dimensionless Mason number Mn is defined to compare the ratio of magnetic and hydrodynamic effect

$$Mn = \frac{\chi^2 B^2}{32\pi\mu_0\eta f}, \quad (1.16)$$

where f is the rotational frequency. When paramagnetic beads form chain structure, its length, expressed by the number of the beads N , is proportional to the square root of Mn , i.e., $N \sim \sqrt{Mn}$.³² N can be tuned via the field and frequency, $N \sim \frac{B}{\sqrt{f}}$. In this dissertation, we focus on ferromagnetic rods instead of paramagnetic beads. Ferromagnetic rods have anisotropic shapes, material compositions, and strong interactions among themselves, which makes their responses to a dynamic field much more complicated than paramagnetic beads.

1.4 Stroke Treatment via Magnetically Powered Motors

A stroke is the rapid loss of brain function due to disturbance in the blood supply to the brain,³⁶ and has become the leading cause of death and the leading cause of disability amongst adults worldwide according to the World Health Organization (WHO). Although intravascular stent by surgery is the most effective way to treat arterial embolism, brain

vessels are normally in sub-millimeter ($100\sim1000\ \mu\text{m}$), which makes this surgery method invalid.³⁷ Despite testing over 70 agents in clinical trials, only one of them has been approved by the Food and Drug Administration (FDA) for the treatment of ischemic stroke. This drug, recombinant tissue plasminogen activator (rt-PA or t-PA), can activate plasminogen to plasmin, which then binds to fibrin and breaks up the blood clot in cerebral blood vessels. t-PA treatment has serious side effects. It has been reported that in about 6-7% cases, the usage of t-PA could cause symptomatic intracranial hemorrhages (SIH).³⁸ In about half cases, t-PA treatment failed to lyse the clot and recanalize the middle cerebral artery.³⁹ As a result, t-PA treatment is rarely suitable for ischemic stroke patients and is used only on about 1% to 2% of them.⁴⁰ In order to improve t-PA treatment, new strategies with better safety and improved effectiveness are needed.

Nanocarrier based drug delivery is promising because of its accurate dose control and precise targeting.⁴¹ Specifically for stroke treatment, thrombolytic drugs was incorporated with magnetic nanoparticles, and delivered to clot site using an external magnetic field.⁴²⁻⁴³ Nanocarrier requires a much smaller amount of drug, which reduces side effects. However, highly specialized nanocarriers need to be developed to load specific drugs, and the drug's effectiveness may be limited by the loading rate of nanocarriers.

In this dissertation, the question we are asking is: once the t-PA drug and nanocarriers are delivered near the blood clot, can we further increase the therapeutic effectiveness through mechanical motions of nanocarriers? In the Chapter 5, the answer is sought through the usage of FMRCs driven by the rotational magnetic field to mechanically agitate the t-PA drug and study its therapeutic effect. We expect that the convection

induced by the rotating FMRCs to enhance diffusion/mass transport of t-PA molecules towards the fibrin surfaces.

1.5 Overview of the Dissertation

The main objective of this dissertation is to study the dynamic behavior and the structural transition of FMRCs under magnetic fields, and to apply it towards stroke treatment.

Chapter 2 will present a study of hydrodynamic propulsion of a single ferromagnetic helix driven by a rotational magnetic field. The governing equation will be presented and the dynamics of the helix will be studied both theoretically and experimentally.

Chapter 3 will present a study of the immediate and the long-term responses of ferromagnetic rod clusters to a static magnetic field.

Chapter 4 will present a study of ferromagnetic rod clusters under changing magnetic fields. First, we will study the dynamic behavior and the structural transition of ferromagnetic rod clusters when the magnetic field is switched from longitudinal direction to transverse direction. Second, we will discuss the behaviors of ferromagnetic rod clusters under a rotational magnetic field.

Chapter 5 will present an application of ferromagnetic rod clusters on the stroke treatment.

Chapter 6 will summarize the dissertation and potential future work.

CHAPTER 2

MAGNETIC PROPULSION OF FERROMAGNETIC-ROD HELIX

Helical structures are widely used for artificial magnetic micro-swimmer as it can be propelled wirelessly with a cork-screw motion, which is linearly controlled by a rotational magnetic field in Low Reynolds number fluids.⁴⁴⁻⁴⁵ Magnetically powered helix has attracted lots of attentions for its potential applications in drug delivery and vascular dredge robots.⁴⁶⁻⁴⁷ Intensive investigations in its fabrication method,^{45, 48-49} dynamic theory,⁵⁰⁻⁵⁵ numerical simulation,⁵⁶⁻⁵⁹ and controlling method under complex magnetic field were conducted.⁶⁰⁻⁶² Typically, magnetic helix is constructed in spiral structure with a circular intersection and smooth skeleton. Either the head or the tail of the structure is made of ferromagnetic materials, such as iron oxide, cobalt or nickel.⁶³ Previously, a rectangular spring-like helix was made of nickel-silicon via alternative steps within a physical deposition method, namely, GLancing-Angle Deposition (GLAD).⁶⁴ This ferromagnetic-rod helix (FMH) is different from previous ones for its square intersection and discontinuous magnetic properties of the skeleton. In this chapter, we first use Newton's dynamic analysis to obtain a hydrodynamic resistant matrix, which expresses the hydrodynamic drag force and torque on a helix with respect to its translational and rotational motion. The optimized geometrical parameters can be found for the maximum translational velocity and propulsion force under a fixed rotational frequency. We then introduce the governing equations of the helix, driven by a rotational magnetic field. The

dynamics of the helix is simulated by solving a 3rd order ODE system while the steady state is derived for the speed limitation of the helix. Finally, fabrication of the helix and experimental observation of such helix will be discussed.

2.1 Hydrodynamic Resistant Matrix of Helix

We consider a rectangular spring coiled with cylindrical arms of radius r and length l . For each arm, the lift angle is θ . The helix is assumed to move with velocity $\vec{U}_1$ and rotate with angular velocity $\vec{\Omega}$ in axial direction $\vec{k}$, of which are shown in Fig. 2.1(a).

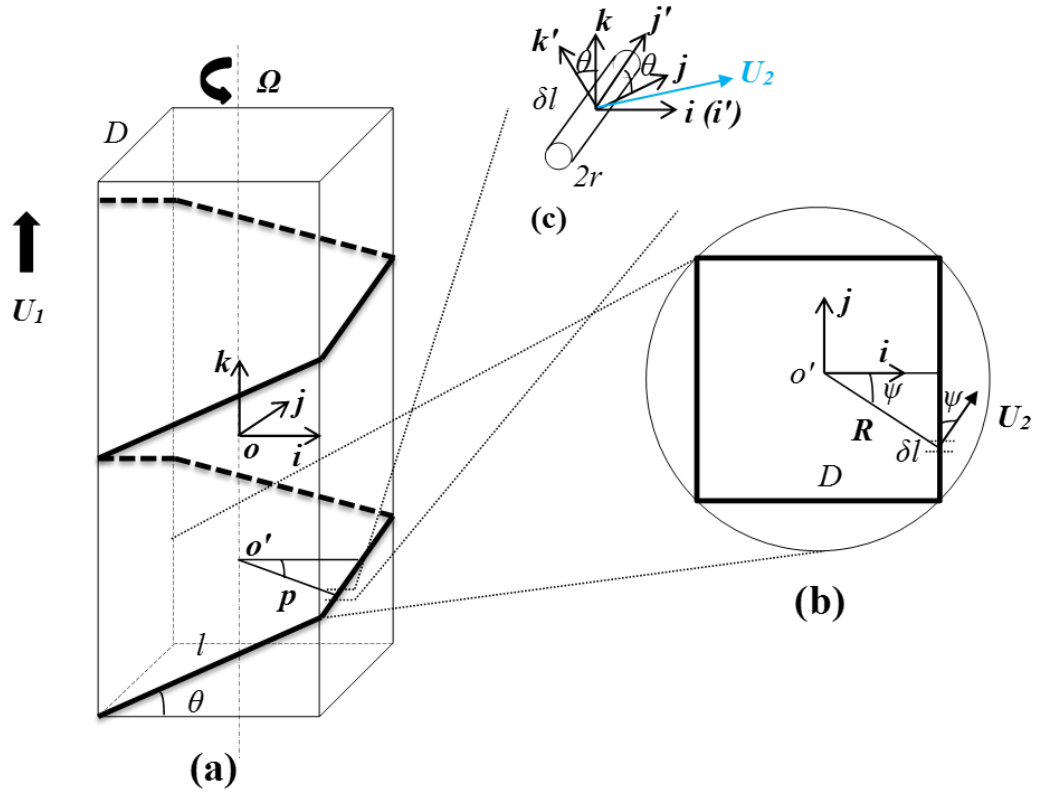


Figure 2.1 Drawings of the rectangular spring with (a) the entire structures, (b) the intersectional view of one period in the structure and (c) one arm of the period.

The projection of the rectangular helix on the axial direction is a square with the side length $D = l \cos \theta$ in the $i-j$ plane (Fig.2.1(b)). The motion of a single arm (e.g., the

right-side arm in Fig. 2.1(b)) includes the linear transition $\vec{U}_1$ in k direction, rotation and spin in i - j plane. Here, i, j, k is in a Cartesian coordinate system with its origin o set on the center of the rectangular spring, each axis perpendicular to the wall of the rectangular shape encapsulating the helix. To study a specific arm in one period, we define o' as the projection of the center point of the arm onto k axis, as shown in Fig. 2.1(b). Figure 2.1(c) illustrates an elementary section along the arm with length δl , and the vector connecting o' and the section is $\vec{p}$ (Fig. 2.1(a)) with its projection $\vec{R}$ in axial direction (Fig. 2.1(b)). The angle between $\vec{p}$ and i axis is ψ , as shown in Fig. 2.1(b). Since $\vec{R}$ is also the rotational radii of the elementary section around k axis, the rotational speed of the section can be expressed as

$$\vec{U}_2 = \vec{\Omega} \times \vec{R} = \frac{\Omega l \cos \theta \tan \psi}{2} \hat{i} + \frac{\Omega l \cos \theta}{2} \hat{j}. \quad (2.1)$$

To investigate the resistance on a specific section δl , we set a new Cartesian system i' - j' - k' attached on the center of the arm, where i' is in the same direction of i , j' is in the long axial direction of the arm, k' is determined by i' and j' . Then the velocity of the section $\vec{v}$ can be expressed as

$$\begin{aligned} \vec{v} &= \vec{U}_1 + \vec{U}_2 = \vec{\Omega} \times \vec{R} = \frac{\Omega l \cos \theta \tan \psi}{2} \hat{i} + \frac{\Omega l \cos \theta}{2} \hat{j} + U_1 \hat{k} \\ &= \frac{\Omega l \cos \theta \tan \psi}{2} \hat{i}' + \left(\frac{\Omega l \cos^2 \theta}{2} + U_1 \sin \theta \right) \hat{j}' + \left(U_1 \cos \theta - \frac{\Omega l \cos \theta \sin \theta}{2} \right) \hat{k}'. \end{aligned} \quad (2.2)$$

Furthermore, the element has a rigid body rotation of the self-spinning,

$$\vec{\omega} = \Omega \hat{k} = \Omega \sin \theta \hat{j}' + \Omega \cos \theta \hat{k}'. \quad (2.3)$$

Assume that the hydrodynamic drag coefficients per unit length parallel and normal to the axis of the cylindrical element are denoted as $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ respectively, we have

$$\varepsilon_{\parallel} = \xi \varepsilon_{\perp}. \quad (2.4)$$

Hancock⁷ (see Tab. 1.1) found $\zeta = 0.5$ for the infinite straight cylinders in unbound fluid. Considering the finite length of the arms, it is reasonable to pick up a high bound of $1 > \zeta > 0.5$ in our case. The resistant force $\vec{f}_h$ on the elementary arm δl due to its transition of Eq. (2.3) is

$$\begin{aligned} \vec{f}_h = & -\delta l \left[\varepsilon_{\perp} \frac{\Omega l \cos \theta \tan \psi}{2} \hat{i} + \varepsilon_{\parallel} \left(\frac{\Omega l \cos^2 \theta}{2} + U_1 \sin \theta \right) \hat{j} + \varepsilon_{\perp} \left(U_1 \cos \theta - \frac{\Omega l \cos \theta \sin \theta}{2} \right) \hat{k} \right] \\ = & -\delta l \left[\varepsilon_{\perp} \frac{\Omega l \cos \theta \tan \psi}{2} \hat{i} + \left(\frac{\Omega l \cos \theta}{2} (\varepsilon_{\parallel} \cos^2 \theta + \varepsilon_{\perp} \sin^2 \theta) + (\varepsilon_{\parallel} - \varepsilon_{\perp}) U_1 \sin \theta \cos \theta \right) \hat{j} \right. \\ & \left. + \left((\varepsilon_{\parallel} - \varepsilon_{\perp}) \frac{\Omega l \cos^2 \theta \sin \theta}{2} + U_1 (\varepsilon_{\parallel} \sin^2 \theta + \varepsilon_{\perp} \cos^2 \theta) \right) \hat{k} \right] \end{aligned} \quad (2.5)$$

Here the ‘*Magnus effect*’ is neglected since the Reynolds number is expected to be small. Then the total resistant $\vec{F}_h$ force on the arm can be integrated with respect to ψ in the range of $[-\pi/4, \pi/4]$

$$\begin{aligned} \vec{F}_h = & \int_{-\pi/4}^{\pi/4} \vec{f}_r d \left(-\frac{l}{2} \tan \psi \right) = - \left(\frac{\Omega l^2 \cos \theta}{2} (\varepsilon_{\parallel} \cos^2 \theta + \varepsilon_{\perp} \sin^2 \theta) + (\varepsilon_{\parallel} - \varepsilon_{\perp}) U_1 l \sin \theta \cos \theta \right) \hat{j} \\ & - \left((\varepsilon_{\parallel} - \varepsilon_{\perp}) \frac{\Omega l^2 \cos^2 \theta \sin \theta}{2} + U_1 l (\varepsilon_{\parallel} \sin^2 \theta + \varepsilon_{\perp} \cos^2 \theta) \right) \hat{k} \end{aligned} \quad (2.6)$$

Now let's consider the hydrodynamic torque on the helix induced by the hydrodynamic force on a single arm. As shown in Fig. 2.1(b), if the helix rotates around the k axis, the rotational center is at the point o' , which is at the same level of the center point of the arm. Therefore, the hydrodynamic torque from an elementary force (Eq. (2.5)) can be expressed as

$$\delta \vec{\Gamma}_f = \vec{p} \times \vec{f}_r, \quad (2.7)$$

where $\vec{p}$ is the vector pointing from o' to the elementary section. From the geometry in Fig. 6-1(a) and (b), $\vec{p}$ can be expressed in i - j - k coordinates

$$\vec{p} = \frac{l \cos \theta}{2} \hat{i} - \frac{l \cos \theta \tan \psi}{2} \hat{j} - \frac{l \sin \theta \tan \psi}{2} \hat{k}. \quad (2.8)$$

Plugging Eqs. (2.5) (2. 8) in Eq. (2. 7), we have

$$\begin{aligned} \vec{\delta \Gamma}_f = & \delta l \left(\frac{\varepsilon_{\perp} U_1 l \tan \psi \cos \theta}{2} - \frac{\varepsilon_{\perp} \Omega l^2 \tan \psi \cos \theta \sin \theta}{4} \right) \hat{i} + \\ & \delta l \left[\frac{\Omega l^2 \cos \theta \sin \theta (\varepsilon_{\parallel} \cos^2 \theta - \varepsilon_{\perp} \cos^2 \theta + \varepsilon_{\perp} \tan^2 \psi)}{4} + \frac{U_1 l \cos \theta (\varepsilon_{\perp} \cos^2 \theta + \varepsilon_{\parallel} \sin^2 \theta)}{2} \right] \hat{j} \cdot \quad (2.9) \\ & + \delta l \left[-\frac{\Omega l^2 \cos^2 \theta (\varepsilon_{\parallel} \cos^2 \theta + \varepsilon_{\perp} \sin^2 \theta + \varepsilon_{\perp} \tan^2 \psi)}{4} - \frac{U_1 l \cos^2 \theta \sin \theta (\varepsilon_{\parallel} - \varepsilon_{\perp})}{2} \right] \hat{k} \end{aligned}$$

Since all the parameters are constant along the arm except ψ , then the total moment by force on the arm to the point o' can be integrated on ψ in $[-\pi/4, \pi/4]$

$$\begin{aligned} \vec{\Gamma}_f = & \int_{-l/2}^{l/2} d\vec{\Gamma}_f = \left[\frac{\Omega l^3 \cos \theta \sin \theta (3\varepsilon_{\parallel} \cos^2 \theta - 3\varepsilon_{\perp} \cos^2 \theta + \varepsilon_{\perp})}{12} + \frac{U_1 l^2 \cos \theta (\varepsilon_{\perp} \cos^2 \theta + \varepsilon_{\parallel} \sin^2 \theta)}{2} \right] \hat{j} \\ & - \left[\frac{\Omega l^3 \cos^2 \theta (3\varepsilon_{\parallel} \cos^2 \theta + 3\varepsilon_{\perp} \sin^2 \theta + \varepsilon_{\perp})}{12} + \frac{U_1 l^2 \cos^2 \theta \sin \theta (\varepsilon_{\parallel} - \varepsilon_{\perp})}{2} \right] \hat{k} \end{aligned} \quad (2.10)$$

Notice that the j component of the torque is not zero, which can be balanced by torque component from the opposite arm. If the helical tail is completely periodic configuration, the number of the arms is $4 \times n$, the sum of j moments is zero, and the helix can be balanced itself. When hydrodynamic forces and torques on all the arms are added together, their components in i and j direction will be canceled due to the symmetry of the structure. As a result, the net force and torque are only in k direction. Multiplying the k components in Eqs. (2.6) and (2.10) with $4n$, the hydrodynamic resistant force and torque on a helix can be eventually expressed in the form of Eq. (1.9)

$$\begin{bmatrix} \vec{F}_h \\ \vec{\Gamma}_h \end{bmatrix} = M_h \begin{bmatrix} \vec{U}_1 \\ \vec{\Omega} \end{bmatrix}. \quad (2.11)$$

Here, M_h is known as a hydrodynamic resistant matrix

$$M_h = \begin{bmatrix} a & b \\ b & c \end{bmatrix}, \quad (2.12)$$

where $a = -4nl(\varepsilon_{\parallel} \sin^2 \theta + \varepsilon_{\perp} \cos^2 \theta)$, $b = 2nl^2(\varepsilon_{\perp} - \varepsilon_{\parallel})\cos^2 \theta \sin \theta$, and

$c = -nl^3\left(\varepsilon_{\perp} \sin^2 \theta + \varepsilon_{\parallel} \cos^2 \theta + \frac{\varepsilon_{\perp}}{3}\right)\cos^2 \theta$. M_h is symmetric to confirm the reciprocal theorem

of Stokes flow.¹⁶ Therefore, the direction of $\vec{U}_1$ is reversed if $\vec{\Omega}$ is in a counter direction.

Optimized design of the helical tail with a spherical head

A helical swimmer consists of a spherical head with diameter d and a helical tail with $4n$ arms of length l . According to Eq. (1.6), the hydrodynamic drag on the head is

$$\vec{F}_D = -3\pi\eta d\vec{U}_1. \quad (2.13)$$

Notice $\varepsilon_{\parallel} < \varepsilon_{\perp}$, ($\zeta < 1$) and the axial propulsion force by a single arm of the helical structure is described for k component in Eq. (2.6). For a static transition in the axial direction, the total forces on the swimmer should be balanced

$$4n\left[(\varepsilon_{\perp} - \varepsilon_{\parallel})\frac{\Omega l^2 \cos^2 \theta \sin \theta}{2} - U_1 l(\varepsilon_{\parallel} \sin^2 \theta + \varepsilon_{\perp} \cos^2 \theta)\right] = 3\pi\eta d U_1, \quad (2.14)$$

Thus, the magnitude of the static velocity $\vec{U}_1$ is

$$U_1 = \frac{2n(\varepsilon_{\perp} - \varepsilon_{\parallel})\Omega l^2 \cos^2 \theta \sin \theta}{4nl(\varepsilon_{\parallel} \sin^2 \theta + \varepsilon_{\perp} \cos^2 \theta) + 3\pi\eta d}. \quad (2.15)$$

According to Eq. (2.15), the transitional velocity $\vec{U}_1$ is proportional to the angular velocity Ω with an upper boundary magnitude ($n \rightarrow \infty$)

$$U_1^{upper} = \frac{(\varepsilon_{\perp} - \varepsilon_{\parallel})\Omega l \cos^2 \theta \sin \theta}{2(\varepsilon_{\parallel} \sin^2 \theta + \varepsilon_{\perp} \cos^2 \theta)}. \quad (2.16)$$

In addition to the turn number, the lift angle θ of the helical arm are critical to optimize the hydrodynamic propulsion of the helix. From Eq. (2.16), we have $\theta = \arctan(0.5\zeta)$, where

$\zeta = \sqrt{1 + \frac{8}{\xi}} - 1$, when the transitional velocity of an infinite long helix reach its maximum value

$$U_1^{\max} = \frac{(1 - \xi)\Omega l \sqrt{\zeta}}{(0.5\xi\zeta + 2)\sqrt{4 + \zeta}}. \quad (2.17)$$

Equations (2.15), (2.16) and (2.17) suggest that the propagating velocity of a helix only depends on how fast it rotates, not on the viscosity of the carrier liquid. The maximum velocity under a fixed angular velocity is determined by the structural parameters n , l and θ . When attached onto the helical tail, the resistant torque on the spherical head (Eq. (1.6)) induced by the rotating motion Ω is

$$\vec{\Gamma}_h = -\pi\eta d^3 \Omega \hat{k}. \quad (2.18)$$

Thus, the total resistant torque on the swimmer regarding to the transitional velocity of Eq. (2.15) is

$$\vec{\Gamma}_R = \left[n\Omega l^3 \cos^2 \theta \left(\varepsilon_{\parallel} \cos^2 \theta + \varepsilon_{\perp} \sin^2 \theta + \frac{\varepsilon_{\perp}}{3} \right) - \frac{4n^2 l^4 \Omega \cos^4 \theta \sin^2 \theta (\varepsilon_{\parallel} - \varepsilon_{\perp})^2}{3\pi\eta d + 4nl(\varepsilon_{\parallel} \sin^2 \theta + \varepsilon_{\perp} \cos^2 \theta)} + \pi\eta d^3 \Omega \right] \hat{k}. \quad (2.19)$$

Therefore, the resistant torque (Eq. (2.19)) is proportional to Ω and greatly reduced by the volume of the swimmer (*e.g.*, l^3 , d^3).

Besides the transitional motion, the helical swimmer is expected to penetrate boundaries, such as liquid interface, bio-membranes, etc., in the practical applications. Its propulsion force F_p can be calculated by assuming $U_1 = 0$ in Eq. (2.15)

$$F_p = 2n(\varepsilon_{\perp} - \varepsilon_{\parallel})\Omega l^2 \cos^2 \theta \sin \theta. \quad (2.20)$$

The propulsion force is proportional to the square of the helical arm length l . Furthermore, there is an optimized lift angle

$$\theta = \arctan \frac{\sqrt{2}}{2} = 35.26^\circ. \quad (2.21)$$

with which the force of penetration reaches its maximum

$$F_p = \frac{4\sqrt{3}}{9} n \Omega l^2 (\varepsilon_{\perp} - \varepsilon_{\parallel}). \quad (2.22)$$

2.2 Helix Powered by a Rotational Magnetic Field

Now we consider a helix that is driven by a rotating magnetic field with the rotational direction in the axial length of the helix. From Newton's Second Law, we have

$$\begin{bmatrix} \vec{F}_m \\ \vec{\Gamma}_m \end{bmatrix} + \begin{bmatrix} \vec{F}_h \\ \vec{\Gamma}_h \end{bmatrix} = \begin{bmatrix} A & 0 \\ 0 & J_k \end{bmatrix} \begin{bmatrix} \dot{\vec{U}}_1 \\ \dot{\vec{\Omega}} \end{bmatrix}, \quad (2.23)$$

where A is the mass and J_k is the rotational inertia in k direction of the helix.

Assume magnetic arms are magnetized in their axial direction with the volume magnetization M , the magnetic moment of a single arm m equals to $\pi r^2 l M$ and can be decomposed into m_1 and m_2 in j and k direction. Defining the included angle between the magnetic field $\vec{B}$ and the i axis (Fig. 2.1(b)), the magnetic torques on one periodic helical structure (four continuous arms) can be calculated by $\vec{m} \times \vec{B}$, of which results are listed in Tab. 2.1.

Table 2.1 Magnetized configuration and the induced torques on a periodic helical structure

	$\vec{M}_1$ in i - j plane	$\vec{\Gamma}_1$ of total 4 arms in k axis	$\vec{M}_2$ in k axis	$\vec{\Gamma}_2$ of total 4 arms in i - j plane
1		$\Gamma_1 = 0$		$\Gamma_2 = 4mB \sin \theta$

2	$\begin{array}{c} \rightarrow \\ \downarrow \quad \uparrow \\ \leftarrow \end{array}$	$\Gamma_1 = 0$	$\begin{array}{c} \times \\ \bullet \quad \bullet \\ \times \end{array}$	$\Gamma_2 = 0$
3	$\begin{array}{c} \rightarrow \\ \downarrow \quad \downarrow \\ \rightarrow \end{array}$	$\Gamma_1 = 2\sqrt{2}mB \cos \theta \sin(\varphi + \pi/4)$	$\begin{array}{c} \times \\ \bullet \quad \times \\ \bullet \end{array}$	$\Gamma_2 = 0$
4	$\begin{array}{c} \leftarrow \\ \\ \rightarrow \end{array}$	$\Gamma_1 = 0$	$\begin{array}{c} \bullet \\ \\ \bullet \end{array}$	$\Gamma_2 = 2mB \sin \theta$
5	$\begin{array}{c} \rightarrow \\ \\ \rightarrow \end{array}$	$\Gamma_1 = 2mB \cos \theta \sin \varphi$	$\begin{array}{c} \times \\ \\ \bullet \end{array}$	$\Gamma_2 = 0$

Table 2.1 illustrates five different combinations of the helical arms, of which magnetized direction (in j and k axis) from the top view (view from one end of the helix) are listed in the second and the fourth columns. The induced magnetic torques $\vec{\Gamma}_1$ (in k direction) and $\vec{\Gamma}_2$ (in i - j plane) are given in the third and fifth columns. $\vec{\Gamma}_1$ drives the helix to rotate in i - j plane and maintain a stable translation in k direction. However, $\vec{\Gamma}_2$ brings the unexpected rotation deviating from the translational direction and leads to the flipping motion of the helix. Thus, only configuration 3 and 5 satisfy to our requirements. Let's first consider the configuration 3 driven by a rotational magnetic field $\vec{B}$ with a constant angular velocity Ω_B and $\nabla \vec{B} = 0$. Multiplying $\vec{\Gamma}_1$ of a single periodic helical structure with n periods, we obtain the magnetic torque on the whole helix $\vec{\Gamma}_m$. Plugging it into Eq. (2.23) and since there is no magnetic force in $\mathbf{k}$ direction, we have the governing equation of helix

$$\begin{bmatrix} 0 \\ 2\sqrt{2}nmB \cos \theta \sin\left(\varphi + \frac{\pi}{4}\right) \end{bmatrix} = - \begin{bmatrix} a & b \\ b & c \end{bmatrix} \begin{bmatrix} U_1 \\ \Omega \end{bmatrix} + \begin{bmatrix} A & 0 \\ 0 & J_k \end{bmatrix} \begin{bmatrix} \dot{U}_1 \\ \dot{\Omega} \end{bmatrix}. \quad (2.24)$$

For steady state, the transitional velocity U_1 and angular velocity Ω are constant and Eq. (2.24) becomes

$$\begin{bmatrix} 0 \\ 2\sqrt{2}nmB\cos\theta\sin\left(\varphi+\frac{\pi}{4}\right) \end{bmatrix} = -\begin{bmatrix} a & b \\ b & c \end{bmatrix} \begin{bmatrix} U_1 \\ \Omega \end{bmatrix}. \quad (2.25)$$

To maintain steady state motion, the exerting magnetic torque also need be a constant.

Thus, an implicit condition is added

$$\dot{\varphi} = \Omega_B - \Omega = 0. \quad (2.26)$$

Equation (2.26) implies the rotation of the helix has to follow the magnetic field to reach a stable motion, *i.e.*, $\Omega = \Omega_B$. The associated translational velocity is

$$U_1 = -\frac{b}{a}\Omega_B = \frac{l(c_N - c_T)\cos^2\theta\sin\theta}{2(c_T\sin^2\theta + c_N\cos^2\theta)}\Omega_B. \quad (2.27)$$

Combining Eqs. (2.25) and (2.27), we also have

$$2\sqrt{2}nmB\cos\theta\sin\left(\varphi+\frac{\pi}{4}\right) = \left(\frac{b^2}{a} - c\right)\Omega_B. \quad (2.28)$$

It is straightforward to know that $\frac{b^2}{a} - c > 0$. On one hand, the phase difference φ is determined as

$$\varphi = \sin^{-1}\left[\frac{(b^2 - ac)\Omega_B}{2\sqrt{2}nmB\cos\theta}\right] - \frac{\pi}{4}. \quad (2.29)$$

On the other hand, the maximum angular velocity the helix can follow is

$$\Omega_B = \sin\left(\varphi + \frac{\pi}{4}\right) \frac{2\sqrt{2}nmB\cos\theta}{b^2 - ac} \leq \frac{2\sqrt{2}nmB\cos\theta}{b^2 - ac}. \quad (2.30)$$

Under such magnetic fields, the translational velocity of the helix reaches the maximum value of

$$U_1 = \frac{2\sqrt{2}nbmB\cos\theta}{b^2 - ac}. \quad (2.31)$$

The upper boundary of the helix motion has been calculated by considering its static motion of Eq. (2.25). Now let's consider the situations where a rotational magnetic field suddenly applied on a resting helix, or the magnetic field suddenly changed when the helix was in a steady state motion. The answer can be given by solving Eq. (2.24) with different initial conditions. Again, we first set up the dynamic relations of phase angle $\varphi(t)$, angular velocity $\Omega(t)$ and the magnetic field rotational speed Ω_B

$$\begin{aligned}\dot{\varphi}(t) &= \Omega_B - \Omega(t) \\ \ddot{\varphi}(t) &= -\dot{\Omega}(t)\end{aligned}\quad (2.32)$$

Plugging Eq. (2.32) into (2.24), we have a coupled ODE system

$$\begin{cases} A\dot{U}_1 = aU_1 - b\dot{\varphi} + b\Omega_B \\ bU_1 = c\dot{\varphi} - 2\sqrt{2}nmB\cos\theta\sin\left(\varphi + \frac{\pi}{4}\right) - c\Omega_B - J_k\ddot{\varphi} \end{cases} \quad (2.33)$$

where $A = 4n\pi r^2 l \rho$, $J_k = \frac{Al^2 \cos^2 \theta}{3}$ and ρ is the mass density of the helix. Equation (2.33)

can be represented by a 3rd order ODE only with respect to φ . A *Runge-Kutta* method is employed to solve the equation. All the parameters used for the simulation are listed in Tab. 2.2.

Table 2.2 Parameters of helix dynamic simulation

Symbol	Name	Value
<i>Helix:</i>		
l	Length of an arm	500 μm
r	Radius of an arm	20 μm
n	Periodic number	2
ρ	Density of the material (Nickel)	8.9 g/cm ³
M	Residual magnetization	10 ⁵ A/m
<i>B field</i>		
f	Rotating frequency	10 Hz
B	Magnetic flux density	20 mT
<i>Carrier liquid:</i>		

η	Dynamic viscosity	1 mPa·s
ξ	Ratio of hydrodynamic coefficients	0.5
Initial Conditions		
φ	Phase difference	$\pi/4$
Ω	Angular velocity	0
U_1	Translational velocity	0

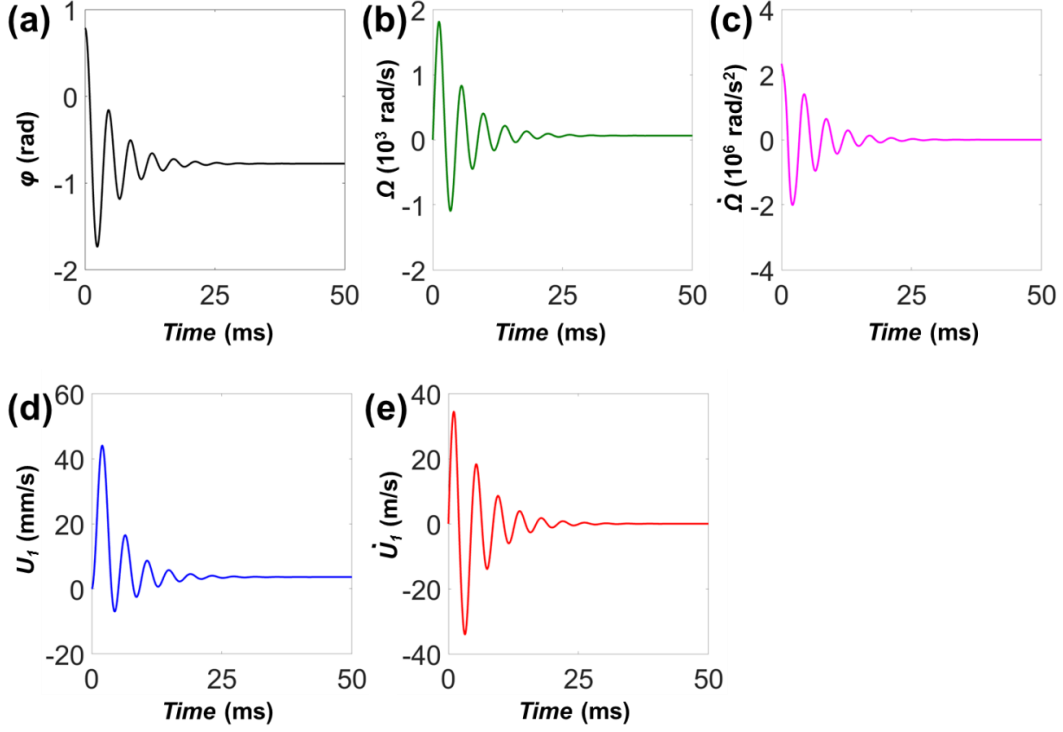


Figure 2.2 Time transient plots of the dynamic parameters of helix (a) Phase angle $\varphi(t)$; (b) angular velocity $\Omega(t)$; (c) angular acceleration $\dot{\Omega}(t)$; (d) translational velocity $U_1(t)$ and (e) translational acceleration $\dot{U}_1(t)$.

Figure 2.2 depicts the transient dynamic parameters in the time domain. From the figure, there are oscillations at the beginning of the magnetic field application. However, they reach to a stable value quickly in approximately 0.025s. This settles the helix into a steady state motion under the driven field. Specifically, $\varphi = 0$, $\Omega = 62.8 \text{ rad/s}$, $\dot{\Omega} = 0 \text{ rad/s}^2$, $U_1 = 3.6 \text{ mm/s}$ and $\dot{U}_1 = 0 \text{ mm/s}^2$ when t approaches infinite.

2.3 Experimental Observation and Discussion

As shown in Fig. 2.3(a-d), a two-turn and eight-arm magnetic helical structure was grown on a polyethylene bead (500 nm) by a multilayer glancing angle deposition (GLAD) technique⁶⁴⁻⁶⁵. GLAD technique is an important extension of oblique angle deposition (OAD), whose details will be introduced in Chapter 4. Compared to OAD technique, the position of a substrate is dynamically changed during GLAD. As a result, complex structures can be fabricated with GLAD⁶⁵⁻⁶⁶. In addition to the complex structures, material composition of the helix can also be controlled from layer to layer, resulting in a multilayer structure. In our experiments, the helical arms changed from nickel (blue) to silicon (green) as a result of exposing the substrate to the different vapor sources (Fig. 2.3(b) and (c)). According to SEM micrographs (Fig. 2.3(e)), the length of the arm is about 500 nm and the width is about 200 nm. After the fabrication, the substrate was placed between two electromagnets for magnetization with $B = 50$ mT for 5-10 minutes, as shown in Fig. 2.3(f). The orientation of the substrate was adjusted so that the nickel arms of the helixes were magnetized along their axial direction, or j direction in Fig. 2.1.

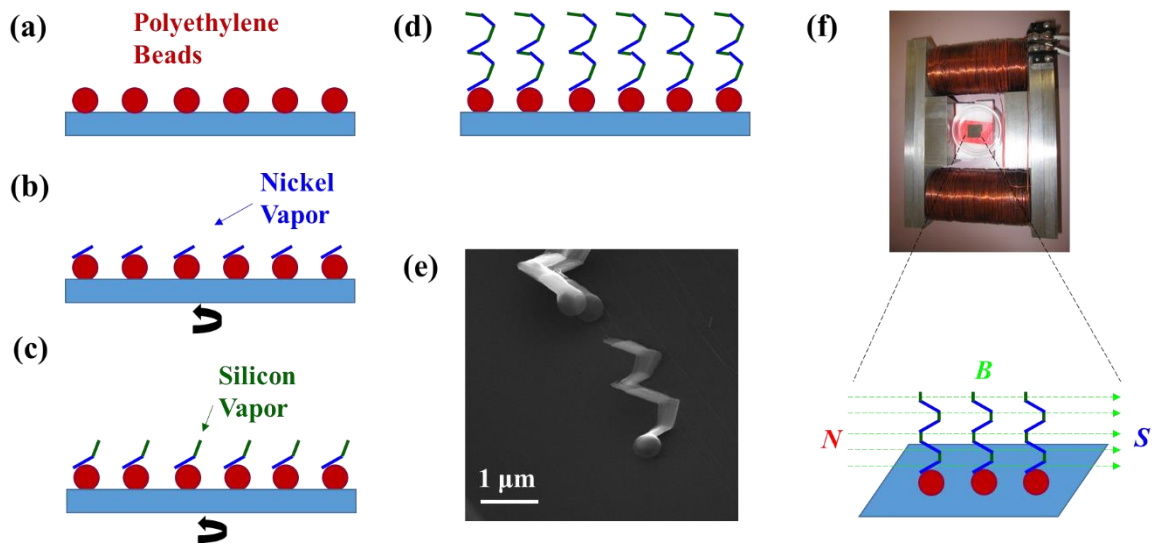


Figure 2.3 The preparation of magnetic helix in steps of (a-d) fabrication by GLAD; (e) characterization by SEM and (f) magnetization by an electromagnet.

The resulting helices were suspended in deionized water and injected into a rectangular PDMS channel with intersectional dimensions of $1000 \times 28 \mu\text{m}^2$. The channel was placed at the center of a custom-made and cubic-like coils, which were orthogonally assembled with three pairs of solenoids in x , y , z directions. The coils were coupled with an optical microscope and a high-speed camera (SLAM Solutions, Phantom v9.1), as shown in Fig. 2.4(a). The rotational magnetic field was generated by the coils in the x - z plane, and the helix is expected to rotate and translate in y direction. Figure 2.4(b) shows a sequence of images of the helix motion in the channel driven by a rotational magnetic field of $B = 30 \text{ mT}$ and $f = 40 \text{ Hz}$. The helix marked in the red circles translates along the channel wall with a stable velocity of $U_1 = 154 \mu\text{m}/\text{second}$.

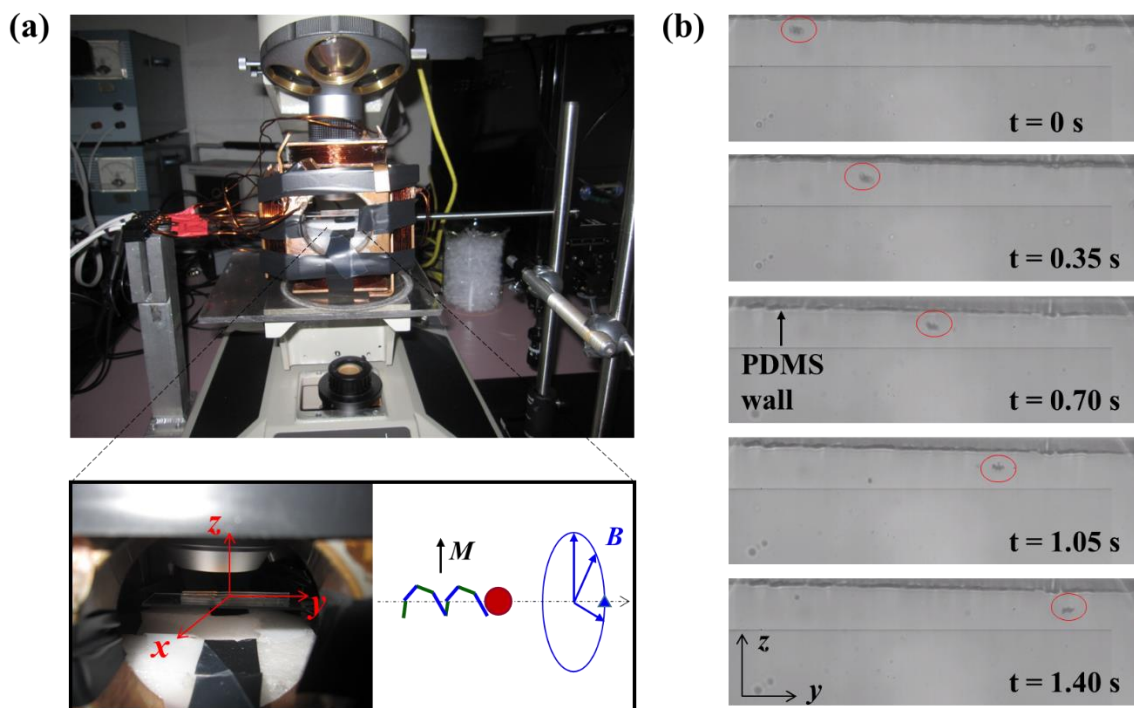


Figure 2.4 The propulsion of magnetic helix driven by a rotational magnetic field (a) The experimental setup; (b) The experimental observation under an optical microscope.

According to Eq. (2.30), the maximum Ω_B the helix can follow is about 24790 Rads/second. Thus, we can assume that the helix is driven by the external magnetic field and reaching its stable velocity, which can be calculated by Eq. (2.15). Since the lift angle θ is unknown, we use Eq. (2.17) to estimate the upper boundary of the helix to be 18 $\mu\text{m/s}$. This value is one order lower than the speed we observed in the experiments. The discrepancy can be explained as following. The object in the red circle (Fig. 2.4(b)) is larger than the helix seen under SEM (Fig. 2.4(e)). The dimensions of the swimmer in Fig. 2.4(b) was around $3 \times 11 \mu\text{m}$. It is very possible that the swimmer is in fact a small cluster of helices. The similar phenomenon has been reported on the small cluster of magnetic chiral structures, of which dynamics depends on the assembly configuration.⁶⁷ According to Eq. (2.17), a helix with 10-time larger size will have its maximum speed of 180 $\mu\text{m/s}$, which is comparable to our observed value of 154 $\mu\text{m/second}$.

2.4 Conclusions

In this chapter, we theoretically investigate the hydrodynamic propulsion of a FMH driven by a rotational magnetic field. The results show that the helix can achieve a stable velocity if it can follow the field. This velocity is proportional to the rotating frequency of the magnetic field. The translation of the helix can be controlled by an external magnetic field.

CHAPTER 3

FERROMAGNETIC-ROD CLUSTER UNDER A STATIC MAGNETIC FIELD

In this chapter, we focus on the dynamic behavior of ferromagnetic microrod clusters (FMRCs) under different magnetic fields. Dynamic response of magnetic micro-/nano- particles suspended in fluids under an external magnetic field has attracted decades of attentions, because of its potential applications in biosensors,⁶⁸⁻⁷⁰ microfluidic actuators,⁷¹⁻⁷⁴ tunable optical and thermal filters,⁷⁵⁻⁷⁹ micro-fiber fabrication,⁸⁰⁻⁸² and programmable smart materials.⁸³⁻⁸⁵ Most of these applications are related to the anisotropic growth of one-dimensional clusters from magnetic particles under an external magnetic field B , which has been studied both experimentally and theoretically.^{17, 21-25, 86-91} In this chapter, we first consider the magnetic energy of a dual-rod system, which is used to explain the structural difference of FMRCs with absence and presence of a static B -field. Then we experimentally demonstrate the immediate response of FMRCs to a static B field associated with this structural transition, which is essentially a rotation-extension coupled motion. A theoretical model based on the extension of a *zig-zag* chain is developed to explain the structural transition. As a result, both the cluster length and orientation can be characterized by a retardation time constant τ , with a relationship $\tau \sim N^2/B$, which agrees well with the experimental results, $\tau \sim N^{2.2 \pm 0.2}/B^{0.8 \pm 0.1}$. Lastly, we study the long chain formation due to the long-term interaction between the extended FMRCs.

3.1 Energy Dependent Configuration of Dual FMRs

The interim structure of a dual FMRs model, from a side-by-side structure to an end-to-end structure, is illustrated in Fig 3.1(a). Two FMRs of length l and diameter d with magnetic moment m , are connected at their ends with an included angle θ . If the FMR is treated as a single magnetic dipole that is concentrated at the center of mass and aligned in the long axial direction of rods, the distance between two dipoles is $r = \left(l \sin \frac{\theta}{2} + d \cos \frac{\theta}{2} \right)$ and the magnetic energy E_m of the dual rods model without B field can be adapted from the dipolar model of Eq. (1.10)

$$E_m = \frac{\mu_0 m M \gamma (\cos \theta - 3)}{32 \left(\gamma \sin \frac{\theta}{2} + \cos \frac{\theta}{2} \right)^3}, \quad (3.1)$$

where M is the magnetization (446 kA/m for bulk Fe_3O_4) and γ is the aspect ratio of the rods. E_m is a function of θ and γ , determined by the configuration of the dual rod model.

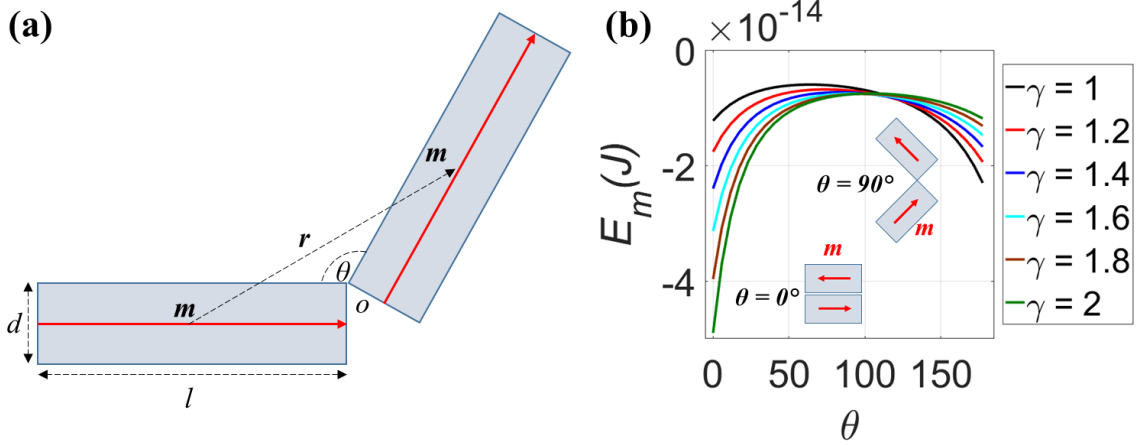


Figure 3.1 Dual FMRs model with the magnetic-dipole concentrated in the rod center with the absence of B field. (a) Configuration of dual rod model; (b) Magnetic energy plot against different configuration.

Figure 3.1(b) depicts the plots of E_m versus θ and γ (solid line). From the calculation, the magnetic energy is relatively low at $\theta = 0^\circ$ and $\theta = 180^\circ$, which means that both the raft-

like and chain-like structure of dual rods are energetically favorable. Furthermore, there is an energy barrier for the rods to overcome from $\theta = 0^\circ$ to $\theta = 180^\circ$, or in the reverse direction. Specifically, the long rods (large γ , green solid line) are more likely arranged side-by-side while the short rods (small γ , black solid line) prefer to attach end-to-end.

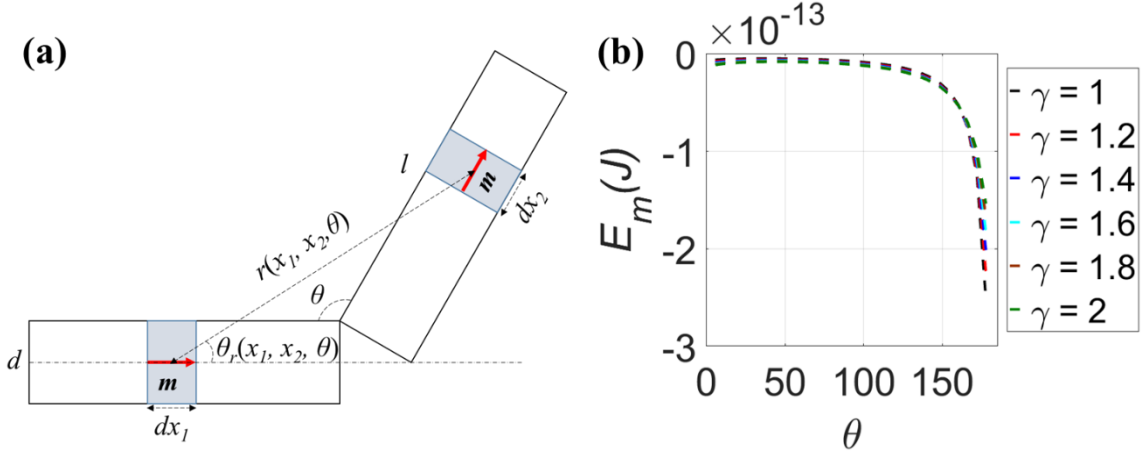


Figure 3.2 Dual FMRs model with the magnetic-dipoles uniformly distributed along the rod with the absence of B field. (a) Configuration of dual rod model; (b) Magnetic energy plot against different configuration.

A more rigorous consideration is to treat each FMR with uniform magnetic dipoles distribution along the long axis direction, as shown in Fig. 3.2(a). For the two arbitrary selected location x_1 and x_2 on each rod, their local dipole moment is $m_{x1} = \pi d^2 M / 4 \cdot dx_1$ and $m_{x2} = \pi d^2 M / 4 \cdot dx_2$ and their distance is $r(x_1, x_2, \theta)$ with orientation $\theta_r(x_1, x_2, \theta)$. Then, the magnetic energy between these two local dipole moments is

$$dE_m = \frac{\mu_0 M^2 d^4 \pi}{64 r^3(x_1, x_2, \theta)} \left[-\frac{1}{2} \cos \theta - \frac{3}{2} \cos(\theta + 2\theta_r(x_1, x_2, \theta)) \right] dx_1 dx_2 \text{ and the total magnetic}$$

energy in the system can be expressed as,

$$E_m = - \int_0^l dx_1 \int_0^l \frac{\mu_0 M^2 d^4 \pi}{64 r^3(x_1, x_2, \theta)} \left[-\frac{1}{2} \cos \theta - \frac{3}{2} \cos(\theta + 2\theta_r(x_1, x_2, \theta)) \right] dx_2 \quad (3.2)$$

where

$$r(x_1, x_2, \theta) = \sqrt{\left(\frac{d}{2} \cot \frac{\theta}{2} + x_1\right)^2 + \left(\frac{d}{2} \cot \frac{\theta}{2} + x_2\right)^2 - 2\left(\frac{d}{2} \cot \frac{\theta}{2} + x_1\right)\left(\frac{d}{2} \cot \frac{\theta}{2} + x_2\right) \cos \theta}$$

$$\theta_r(x_1, x_2, \theta) = \arccos \left(\frac{\left(\frac{d}{2} \cot \frac{\theta}{2} + x_1\right)^2 + r^2 - \left(\frac{d}{2} \cot \frac{\theta}{2} + x_2\right)^2}{2r\left(\frac{d}{2} \cot \frac{\theta}{2} + x_1\right)} \right)$$

Figure 3.2(b) plots the numerical calculation of E_m as function of θ for different γ values (dash line). For different rod aspect ratio γ , the trend of the magnetic energy is almost same. Specifically, the magnetic energy remains constant from $\theta = 0^\circ$ to $\theta = 90^\circ$, then it monotonously and rapidly decreases until $\theta = 180^\circ$. Therefore, the chain-like configuration of dual FMRs is more stable than the raft-like configuration. It is preferable for the rods to spread to a single-rod chain structure with little energy barrier.

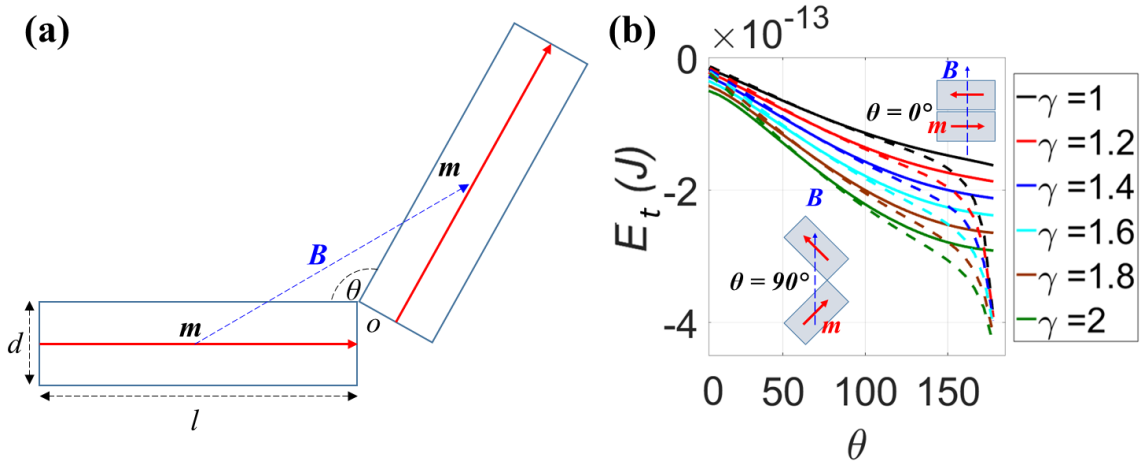


Figure 3.3 Dual FMRs model with the presence of a magnetic field ($B = 0.2$ T). (a) Configuration of dual rod model; (b) Magnetic energy plot against different configuration.

When an external B field is applied, as discussed in Section 1.2 (Eq. (1.13)), an additional dipole-field energy E_B needs be considered. In particular, as shown in Fig.

3.3(a), when the B field is parallel to the center-to-center direction of both rods, based on Eq. (1.12), E_B can be expressed as

$$E_B = 2mB \left(1 - \sin \left(\frac{\theta}{2} \right) \right). \quad (3.3)$$

Figure. 3.3(b) shows the total magnetic energy of the single-dipole model (solid curves) and multi-dipole model (dash curves) under a static magnetic field $B = 0.2$ T. For both models, the magnetic energy E_t decreases monotonously when θ changes from 0° to 180° with no energy barrier. Combining the results of Figs. 3.1-3.3, the included angle θ between FMRs can be tuned by an external B field, resulting in an appreciable extension of FMRC.

3.2 Immediate Response of FMRCs to a Static Magnetic field

Ferromagnetic microrods were synthesized by a solvent-thermal method.⁹² The products were first annealed in air to remove the organic compounds, and further annealed in ethanol/ N_2 to form Fe_3O_4 . $Fe(NO_3)_3 \cdot 9H_2O$ (0.7575 g). Glucose was thoroughly dissolved into ethylene glycol (75 ml). The mixture was transferred into a 100 ml Teflon-lined stainless steel autoclave and maintained at a temperature of $220^\circ C$ for 12 h. The product was collected by centrifugation, washed twice with absolute ethanol, and then dried in an oven at $65^\circ C$ overnight. The microrod-shaped precursors were annealed at $600^\circ C$ for 2 h in air to obtain $\alpha-Fe_2O_3$ microrods. Finally, the Fe_3O_4 microrods were prepared by annealing the $\alpha-Fe_2O_3$ rods at $350^\circ C$ for 1 h in ethanol-carried N_2 flow.

Scanning electron microscope (SEM) image in Fig. 3.4(a) reveals that each rod is a porous cylinder with hemispherical ends. The crystal structures of as-synthesized FMRs were characterized by an X-ray diffractometer (PANalytical X'Pert PRO MRD) with a $Cu K\alpha$ source ($\lambda = 1.5405980 \text{ \AA}$) at 45 kV and 40 Ma (Fig. 3.4(b)). The diffraction angle

scanning range was from 15° to 70° at an angular step of 0.01° . Magnetic properties of as-synthesized Fe_3O_4 microrods were measured at room temperature via a Vibrating Sample Magnetometer (MicroSense Model EZ7) with a 2.15 T electromagnet (Fig. 3.4(c)). The magnetic moment of the sample was measured over a range of applied fields from -1.5 to $+1.5$ kOe. The measurements were conducted in step field mode at a step size of 250 Oe s^{-1} . The hysteresis loop demonstrated that the residual magnetization of each rod was $m = 20 \text{ emu}\cdot\text{g}^{-1}$ (or 10^5 A/m). Additionally, the statistics on the rod diameter d , length l and aspect ratio γ shown in Fig. 3.4 (d)-(f) indicate $d = 0.35 \pm 0.09 \mu\text{m}$, $l = 1.00 \pm 0.25 \mu\text{m}$ and $\gamma = l/d = 2.9 \pm 0.4$.

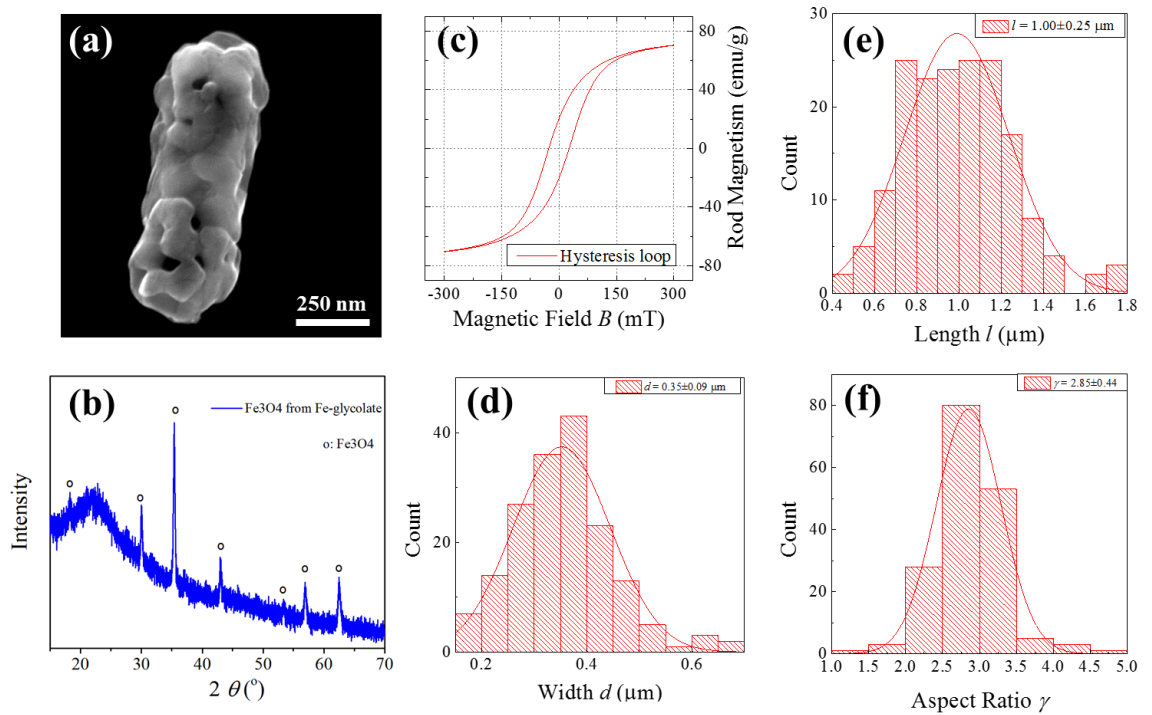


Figure 3.4 Fabrication and characterization of Fe_3O_4 micro rod (a) SEM picture of a single FMR; (b) XRD results of fabricated FMR; (c) Hysteresis loop of FMR sample; (d) Diameter distribution of rods; (e) Length distribution of rods and (f) Aspect ratio distribution of rods.

The rods were suspended in deionized water to achieve a mass concentration of $0.1 \text{ mg}\cdot\text{ml}^{-1}$, corresponding to a volume fraction $\phi \approx 2 \times 10^{-5}$. A $10 \mu\text{l}$ droplet of rod suspension

was dispensed in a well on a clean silicon substrate and covered by a glass slide. The well was made of a 100- μm thick ring-shaped plastic spacer and had a 12.7 mm inner diameter. A static magnetic field was generated by a pair of solenoids (Air-core Solenoid #14825, Science Source, Waldoboro, ME). Through an optical microscope (Mitituya FS110), most of the rod clusters were suspended uniformly in the suspension when $B = 0$ (Fig. 3.5(a)). When a B -field ($B = 0.2$ mT) was applied, the clusters quickly transformed from compact circle-like dots into linear chains along B -field direction (Fig. 3.5(b)). Such a process was recorded at 200 fps by a high-speed CCD camera (SLAM Solutions, Phantom v9.1). From the video, the clusters maintained separation from each other and no cluster-cluster aggregation was observed.

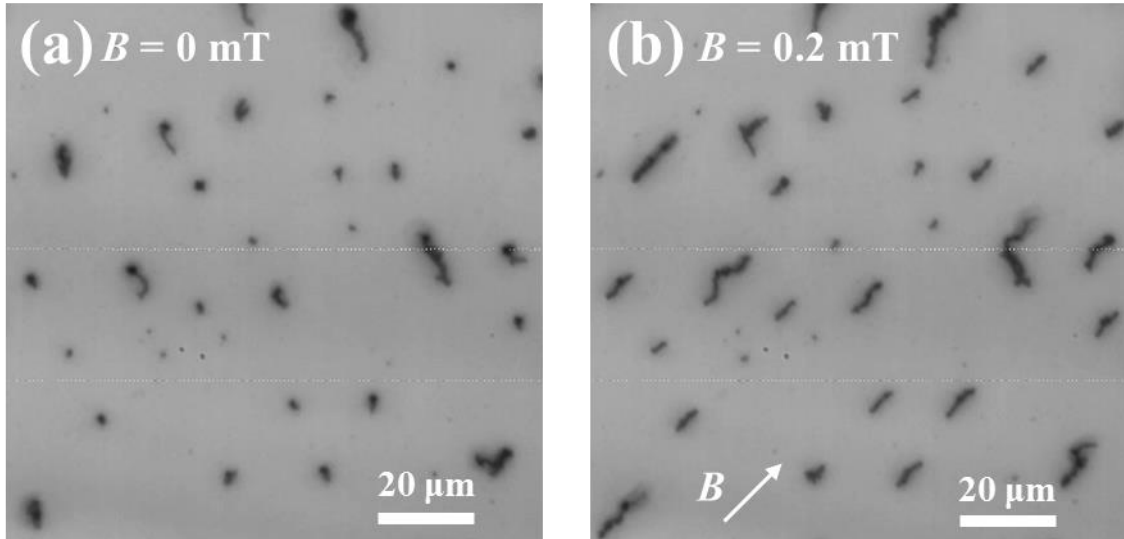


Figure 3.5 An optical microscope image of rod clusters at (a) $B = 0$ mT and (b) $B = 0.2$ mT. The B -field direction is indicated as a white arrow.

Figure 3.6(a) shows the snapshots of an extension process of a FMRC at every 10 ms under $B = 1$ mT. The first frame shows the initial appearance of the FMRC, which was a circular shape ($t = 0$ ms); when $B = 1$ mT was applied (in the direction of the white arrow), the cluster first transformed into a crescent shape ($t = 10$ and 20 ms), then the crescent was

opened to form a short arc ($t = 30, 40$, and 50 ms), and eventually the arc was extended to a straight chain ($t = 60, 70, 80$, and 90 ms). During this configurational change, the orientation of the cluster kept on following the B -field direction as indicated by red arrows in Fig. 3.6(a). To quantitatively characterize the dynamics of the cluster, we defined λ to be the normalized length of the cluster at time t , $\lambda = \frac{L}{L_s}$, where L is the instant length and L_s is the saturated (maximum) length of the cluster chain, and the orientation of the cluster φ is the included angle between the cluster (indicated as red arrows) and the B -field.

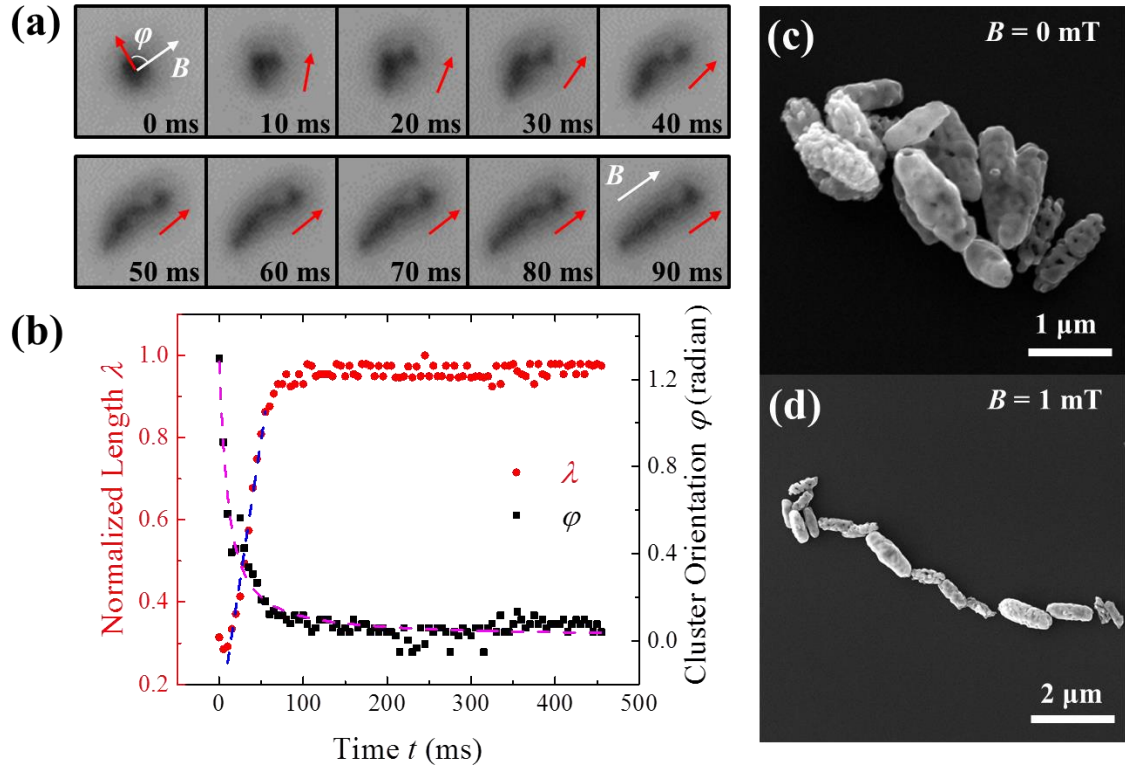


Figure 3.6 Motion analysis on a single FMRC (a) Representative video frames of the extension-rotation coupling motion of a FMRC with $L_s = 9 \mu\text{m}$ at $B = 1$ mT. (b) The plots of the normalized length λ (red circle) and the orientation φ (black square) with respect to time t , extracted from the magnetic cluster shown in (a). The dash curves are the fitting results. Representative SEM images of a FMRC at (c) $B = 0$ mT, and (d) $B = 1$ mT.

Figure 3.6(b) plots λ and φ versus time t extracted from the video's frames (Fig. 3.6(a)). When t increases from 0 to 60 ms, λ increases sharply from its initial value around 0.3 to 0.9. When $t > 60$ ms, λ gradually approaches to a constant value of 0.971. Eventually ($t > 100$ ms), λ fluctuates around this constant value. On the other hand, φ decreases from 1.3 concavely, approaching to 0, when t changes from 0 ms to 150 ms. At $t > 150$ ms, φ fluctuates around $\varphi = 0$. Both the fluctuations of λ and φ at large t are caused by the Brownian fluctuation of the magnetic chain.⁹³ Both Fig. 3.6(a) and (b) reveal the dynamic transformation of the cluster to be an extension-rotation coupled motion. Such a cluster extension and reorientation are caused by the re-arrangement of the rods in the cluster during the application of the external B -field. This is indirectly confirmed by the SEM images of FMRCs with and without the presence of B -field, which are shown in Fig. 3.6(c) and (d), respectively. These SEM samples were prepared by air-drying the FMRC suspensions on the silicon substrates under $B = 0$ mT and $B = 1$ mT, respectively. When $B = 0$ mT, Fig. 3.6(c) shows that the rods are stacked side-by-side to form a raft-like cluster while some rods may form multiple layers on top of the “raft”. This indicates that the rods prefer to pack closely along their long axes, and form a relatively small cluster size. Such a structural feature is consistent to the previous experimental observation and simulation.²⁹⁻

³¹ When $B = 1$ mT, the cluster in Fig. 3.6(d) consists mostly of a single chain with adjacent rods linked end-to-end, which is predicted by the Monte Carlo simulation.¹⁹ Only a few small rods are packed side by side at the ends of the chain, either due to the capillary effect during the drying process, or their strong magnetic interactions.

3.3 Theoretical Model and Dynamic Scaling of Linear Cluster Formation

The dynamic behavior under an external B -field shown in Fig. 3.6(a) is due to the configuration change of FMRCs, which is revealed by Fig. 3.6(c) and (d). This can be treated as an unfolding process. Such unfolding dynamics of scaffolding structures widely exists in biomaterials from micrometer scale to molecular level, such as in polymers,⁹⁴⁻⁹⁵ and proteins.⁹⁶⁻⁹⁸ They have been closely connected to their viscoelasticity. Theoretically, the unfolding process of these biomaterials are described by either a freely-jointed chain model,⁹⁹ or a worm-like chain model.¹⁰⁰ Similarly, the λ and φ curves (Fig. 3.6(b)) exhibit the typical viscoelastic features in response to the external B -field, and the SEM images shown in Fig. 3.6(c) and (d) imply that the extended cluster behaves like a freely-jointed chain based on magnetic interaction. Thus, we propose a freely-jointed chain model to describe this dynamic process.

Figure 3.7(a) illustrates the basic idea of the model with a cluster of three FMRCs. When $B = 0$ mT, the three FMRCs initially form a side-by-side cluster, with the adjacent magnetic moment $\vec{m}$ pointing to the opposite direction (left sketch in Fig. 3.7(a), magnetic dipole indicated by the “+” and “-” signs). When an external B -field is applied, both the FMRCs and the orientation of the cluster (center-to-center direction of FMRCs as indicated by the dash-dotted lines in the middle sketch of Fig. 3.7(a)) are driven to align with the B -field direction, and the cluster becomes a *zig-zag* chain. After sufficient time, the cluster is extended to a linear chain cluster as shown in the right sketch of Fig. 3.7(a). Thus, the extension and reorientation of the FMRCs is essentially caused by the spinning of each FMRC and the rotation of the entire cluster, respectively. The two rotatory motions are associated with two angles, the angle between the cluster axis and the B -field direction φ ,

and the included angle between the long axis of the rod and the principle axis of the chain θ , as indicated in Fig. 3.7(a). During the extension, both φ and θ keep decreasing while the cluster translates from a side-by-side chain to an end-to-end chain aligned in the direction of the B -field.

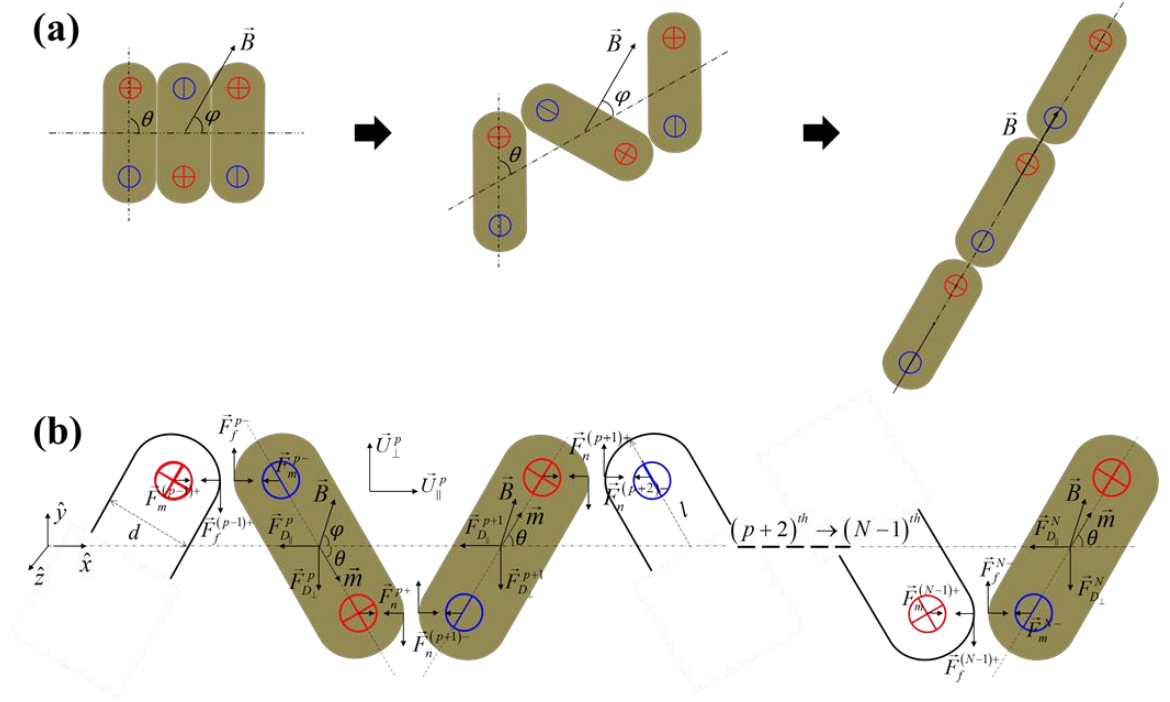


Figure 3.7 Schematic sketch of the coupled motion of a FMRC driven by a static magnetic field. (a) The proposed dynamic process for a side-by-side chain to be extended to an end-to-end chain *via* a zig-zag chain model triggered by an external B -field. (b) Force and torque analysis on a pair of the p^{th} and $(p+1)^{\text{th}}$ rods (color filled, $1 \leq p \leq N - 2$), and the N^{th} rod in the half chain at any time t .

To account for the magnetic interactions between FMRs and to simplify the governing equations, we make the following assumptions: (i) Each rod has the same shape, dimension and magnetic moment m along its long axis; (ii) All the rods in one cluster are

arranged in a *zig-zag* chain structure with the same θ at any time t ; (iii) There is no translational motion of the entire magnetic cluster due to the uniformity of magnetic field ($\nabla B = 0$); (iv) The magnetic interactions among clusters are neglected due to the low volume fraction of rods ($\phi \approx 2 \times 10^{-5}$); (v) Each cluster consists of $2N+1$ (or $2N$) FMRs, so that we only need to analyze the dynamics of FMRs in one half of the cluster due to the symmetry of the *zig-zag* chain.

Since the magnetic moment $\vec{m}$ of two neighboring rods has different orientation, we shall consider the rods in pairs, *i.e.*, the p^{th} rod and the $(p+1)^{\text{th}}$ rod as shown in Fig. 3.7 (b). At the center of the p^{th} ($(p+1)^{\text{th}}$) rod, there are hydrodynamic force components $\vec{F}_{D_{\perp}}^p$ ($\vec{F}_{D_{\perp}}^{p+1}$) and $\vec{F}_{D_{\parallel}}^p$ ($\vec{F}_{D_{\parallel}}^{p+1}$), which are perpendicular and parallel to the principle axis of the cluster. According to Eq. (1.7), $\vec{F}_{D_{\parallel}}^p = -\varepsilon_{\parallel} l \vec{U}_{\parallel}^p$ and $\vec{F}_{D_{\perp}}^p = -\varepsilon_{\perp} l \vec{U}_{\perp}^p$, where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ is the hydrodynamic drag coefficients per unit length in the direction of $\vec{U}_{\parallel}^p$ and $\vec{U}_{\perp}^p$, and $\vec{U}_{\parallel}^p$ and $\vec{U}_{\perp}^p$ is parallel and perpendicular velocity with respect to the chain axis, respectively, $\vec{U}_{\parallel}^p = -pl\dot{\theta} \sin \theta \hat{x}$ and $\vec{U}_{\perp}^p = -pl\dot{\phi} \cos \theta \hat{y}$. Based on a magnetic dipole model,¹⁹ two magnetic force $\vec{F}_m^{p+}$ and $\vec{F}_m^{p-}$ (note that $F_m^{p+} = F_m^{p-} = F_m$) at the + and - ends are presented due to the magnetic polar attraction of the adjacent ends. There are also a normal force $\vec{F}_n^{p+}$ (or $\vec{F}_n^{p-}$) and a frictional force $\vec{F}_f^{p+}$ (or $\vec{F}_f^{p-}$) exerted at the interfaces of the + (or -) end due to the contacting interaction and relative motional tendency between the neighboring rods. Under hydrodynamic equilibrium for a low Reynold number fluid, we have,

$$\vec{F}_n^{p+} + \vec{F}_n^{p-} + \vec{F}_{D_{\parallel}}^p = 0, \quad (3.4)$$

$$\vec{F}_f^{p+} + \vec{F}_f^{p-} + \vec{F}_{D_\perp}^p = 0, \quad (3.5)$$

$$\vec{\Gamma}_m^p + \vec{\Gamma}_r^p = 0, \quad (3.6)$$

where $\vec{\Gamma}_m^p$ is the magnetic driven torque $\vec{\Gamma}_m^p = \vec{m} \times \vec{B} = mB \sin(\varphi + \theta) \hat{z}$, and $\vec{\Gamma}_r^p$ is the

resistant torque, $\vec{\Gamma}_r^p = -\left\{ \left(F_f^{p-} + F_f^{p+} \right) \frac{l}{2} \cos \theta + \left[\left(F_n^{p-} - F_m^{p-} \right) + \left(F_n^{p+} - F_m^{p+} \right) \right] \frac{l}{2} \sin \theta \right\} \hat{z}$.

Similarly equations can be derived for the $(p+1)^{\text{th}}$ rod, but with different expressions for

$$\vec{\Gamma}_m^{p+1} = mB \sin(\varphi - \theta) \hat{z}$$

$$\text{and } \vec{\Gamma}_r^{p+1} = -\left\{ \left(F_f^{(p+1)-} + F_f^{(p+1)+} \right) \frac{l}{2} \cos \theta - \left[\left(F_n^{(p+1)-} - F_m^{(p+1)-} \right) + \left(F_n^{(p+1)+} - F_m^{(p+1)+} \right) \right] \frac{l}{2} \sin \theta \right\} \hat{z}$$

. Furthermore, for the p^{th} and $(p+1)^{\text{th}}$ rod pair, one has $\vec{\Gamma}_m^p + \vec{\Gamma}_m^{p+1} = -(\vec{\Gamma}_r^p + \vec{\Gamma}_r^{p+1})$ and

$\vec{\Gamma}_m^p - \vec{\Gamma}_m^{p+1} = -(\vec{\Gamma}_r^p - \vec{\Gamma}_r^{p+1})$. By considering the fact that $F_f^{p+} = F_f^{(p+1)-}$, $F_n^{p+} = F_n^{(p+1)-}$,

$F_m^{p+} = F_m^{(p+1)-}$, we have

$$2mB \sin \varphi \cos \theta = \left(F_f^{p-} + 2F_f^{(p+1)-} + F_f^{(p+1)+} \right) \frac{l}{2} \cos \theta - \left(F_n^{(p+1)+} - F_n^{p-} \right) \frac{l}{2} \sin \theta, \quad (3.7)$$

$$\begin{aligned} 2mB \cos \varphi \sin \theta = & \left[\left(F_n^{(p+1)+} - F_m^{(p+1)+} \right) + 2 \left(F_n^{(p+1)-} - F_m^{(p+1)-} \right) + \left(F_n^{p-} - F_m^{p-} \right) \right] \frac{l}{2} \sin \theta \\ & - \left(F_f^{(p+1)+} - F_f^{p-} \right) \frac{l}{2} \cos \theta \end{aligned} \quad (3.8)$$

In addition, by summarizing Eqs. (3.4) and (3.5) from the $(p+1)^{\text{th}}$ rod to the N^{th} rod, respectively, and considering the force equilibrium at the N^{th} rod as shown Fig. 3.7(b), we

have $-\vec{F}_f^{(p+1)-} = \sum_{k=p+1}^N \vec{F}_{D_\perp}^k$ and $-\vec{F}_n^{(p+1)-} + \vec{F}_m^{(p+1)-} = \sum_{k=p+1}^N \vec{F}_{D_\parallel}^k$. Therefore, Eqs. (3.7) and (3.8)

becomes

$$2mB \sin \varphi \cos \theta = \left(\sum_{k=p+2}^N F_{D_\perp}^k + 2 \sum_{k=p+1}^N F_{D_\perp}^k + \sum_{k=p}^N F_{D_\perp}^k \right) \frac{l}{2} \cos \theta - \left(F_n^{(p+1)+} - F_n^{p-} \right) \frac{l}{2} \sin \theta, \quad (3.9)$$

$$2mB \cos \varphi \sin \theta = \left(\sum_{k=p}^N F_{D_\parallel}^k + 2 \sum_{k=p+1}^N F_{D_\parallel}^k + \sum_{k=p+2}^N F_{D_\parallel}^k \right) \frac{l}{2} \sin \theta - \left(F_f^{(p+1)+} - F_f^{p-} \right) \frac{l}{2} \cos \theta. \quad (3.10)$$

For **2N+1 FMRs** model, the cluster has one single rod at its center and N rods on both of its sides evenly. Due to the symmetry of the system, we only need to consider the right half of the cluster. If N is an odd number, we need include the central rod (denoted as 0th rod) in the right part of the cluster in order to apply Eqs. (3.9) and (3.10), which are based on the unit pair of rods.

$$(N+1)mB \sin \varphi \cos \theta = \sum_{p=1}^N \sum_{k=p}^N F_{D_\perp}^k l \cos \theta + F_n^{0-} \frac{l}{2} \sin \theta, \quad (3.11)$$

$$(N+1)mB \cos \varphi \sin \theta = \sum_{p=1}^N \sum_{k=p}^N F_{D_\parallel}^k l \sin \theta + F_f^{0-} \frac{l}{2} \cos \theta. \quad (3.12)$$

Applying the same procedure on the left part of the cluster (including the central rod as well), we get the exactly the same expressions of Eqs. (3.11) and (3.12). Since the torques on the central rod are employed twice for the calculation, we need to remove them one time when we added the torque relations of the both sides to estimate the relations on the entire cluster

$$2(N+1)mB \sin \varphi \cos \theta - mB \sin(\varphi + \theta) = 2 \sum_{p=1}^N \sum_{k=p}^N F_{D_\perp}^k l \cos \theta - F_f^{0-} l \cos \theta, \quad (3.13)$$

$$2(N+1)mB \cos \varphi \sin \theta - mB \sin(\varphi + \theta) = 2 \sum_{p=1}^N \sum_{k=p}^N F_{D_{\parallel}}^k l \sin \theta - F_n^{0-} l \sin \theta. \quad (3.14)$$

Plug in all the expressions of the forces (i.e., $F_{D_{\parallel}}^p = -\eta \varepsilon_{\parallel} p l \dot{\theta} \sin \theta$ and $\vec{F}_{D_{\perp}}^p = -\eta \varepsilon_{\perp} p l \dot{\phi} \cos \theta$) in Eqs. (3.13) and (3.14)

$$mB \sin \varphi \cos \theta - \frac{mB}{2N} \cos \varphi \sin \theta = \left(-\frac{N^2}{3} - \frac{N}{4} + \frac{1}{12} \right) \eta \varepsilon_{\perp} \dot{\phi} l^2 \cos^2 \theta, \quad (3.15)$$

$$mB \cos \varphi \sin \theta - \frac{mB}{2N} \sin \varphi \cos \theta = \left(-\frac{N^2}{3} - \frac{N}{4} + \frac{1}{12} \right) \eta \varepsilon_{\parallel} \dot{\theta} l^2 \sin^2 \theta. \quad (3.16)$$

When N is big enough (e.g., $N > 5$), the terms regarding to N with lower exponents can be ignored in the both sides of Eqs. (3.15) and (3.16), then we have

$$\dot{\phi} = -\frac{3mB \sin \varphi}{\varepsilon_{\perp} \eta N^2 l^2 \cos \theta}, \quad (3.17)$$

$$\dot{\theta} = -\frac{3mB \cos \varphi}{\varepsilon_{\parallel} \eta N^2 l^2 \sin \theta}. \quad (3.18)$$

If N is an even number, we need exclude the central rod (denoted as 0^{th} rod) in the right part of the cluster and apply Eqs. (3.9) and (3.10) on the right cluster

$$NmB \sin \varphi \cos \theta = \sum_{p=2}^N \sum_{k=p}^N F_{D_{\perp}}^k l \cos \theta + \sum_{k=1}^N F_{D_{\perp}}^k \frac{l}{2} \cos \theta + F_n^{1-} \frac{l}{2} \sin \theta, \quad (3.19)$$

$$NmB \cos \varphi \sin \theta = \sum_{p=2}^N \sum_{k=p}^N F_{D_{\parallel}}^k l \sin \theta + \sum_{k=1}^N F_{D_{\parallel}}^k \frac{l}{2} \sin \theta + F_f^{1-} \frac{l}{2} \cos \theta. \quad (3.20)$$

Due to the symmetry of the system, the summation of rod pairs over the whole cluster equals to twice of Eqs. (3A.9) and (3A.9) with the complement of the central rod

$$2NmB \sin \varphi \cos \theta + mB \sin(\varphi - \theta) = 2 \sum_{p=2}^N \sum_{k=p}^N F_{D_{\perp}}^k l \cos \theta + 2F_f^{1-} l \cos \theta, \quad (3.21)$$

$$2NmB \cos \varphi \sin \theta + mB \sin(\varphi - \theta) = 2 \sum_{p=2}^N \sum_{k=p}^N F_{D_{\parallel}}^k l \sin \theta + 2F_f^{1-} l \cos \theta. \quad (3.22)$$

Plug in all the expressions of the forces in Eqs. (3.11) and (3.12), and neglect the terms with respect to the lower-order of N , we will obtain the same expressions of Eq. (3.17) and (3.18).

For **2N FMRs** model, the cluster has its center on the joint of the two central rods with N rods on its both sides evenly. If N is an odd number, we exclude the first rod (denoted as 1st rod) in the right part of the cluster and then sum Eqs. (3.9) and (3.10) of the rest pairs of the rods

$$(N-1)mB \sin \varphi \cos \theta = \sum_{p=2}^N \sum_{k=p}^N F_{D_{\perp}}^k l \cos \theta - \sum_{k=2}^N F_{D_{\perp}}^k \frac{l}{2} \cos \theta + F_n^{2-} \frac{l}{2} \sin \theta, \quad (3.23)$$

$$(N-1)mB \cos \varphi \sin \theta = \sum_{p=2}^N \sum_{k=p}^N F_{D_{\parallel}}^k l \sin \theta - \sum_{k=2}^N F_{D_{\parallel}}^k \frac{l}{2} \sin \theta + F_f^{2-} \frac{l}{2} \cos \theta. \quad (3.24)$$

Similarly, the summation on the whole cluster is the double of Eqs. (3.23) and (3.24), adding the corresponding relations of the torques on the central pair of the rods

$$2NmB \sin \varphi \cos \theta = 2 \sum_{p=2}^N \sum_{k=p}^N F_{D_{\perp}}^k l \cos \theta + \sum_{k=1}^N F_{D_{\perp}}^k l \cos \theta + \sum_{k=2}^N F_{D_{\parallel}}^k l \sin \theta, \quad (3.25)$$

$$2NmB \cos \varphi \sin \theta = 2 \sum_{p=2}^N \sum_{k=p}^N F_{D_{\parallel}}^k l \sin \theta + \sum_{k=2}^N F_{D_{\perp}}^k l \cos \theta + \sum_{k=1}^N F_{D_{\parallel}}^k l \sin \theta. \quad (3.26)$$

Notice that the expressions of the forces are different from 2N+1 FMRs model. Here, we

have $F_{D_{\parallel}}^p = -\eta \varepsilon_{\parallel} \left(p - \frac{1}{2} \right) l \dot{\theta} \sin \theta$ and $\vec{F}_{D_{\perp}}^p = -\eta \varepsilon_{\perp} \left(p - \frac{1}{2} \right) l \dot{\phi} \cos \theta$. Plug the expressions of

the forces in Eqs. (3.25) and (3.26),

$$mB \sin \varphi \cos \theta = - \left(\frac{N^2}{3} - \frac{1}{12} \right) \eta \varepsilon_{\perp} \dot{\phi} l^2 \cos^2 \theta - \left(\frac{N}{4} - \frac{1}{4N} \right) \eta \varepsilon_{\parallel} \dot{\theta} l^2 \sin^2 \theta, \quad (3.27)$$

$$mB \cos \varphi \sin \theta = -\left(\frac{N^2}{3} - \frac{1}{12}\right) \eta \varepsilon_{\parallel} \dot{\theta} l^2 \sin^2 \theta - \left(\frac{N}{4} - \frac{1}{4N}\right) \eta \varepsilon_{\perp} \dot{\phi} l^2 \cos^2 \theta. \quad (3.28)$$

Neglect the terms with respect to the lower-order N , we will obtain the same expressions of Eqs. (3.17) and (3.18). If N is an even number, we directly apply the Eqs (3.9) and (3.10) on the entire cluster,

$$2NmB \sin \varphi \cos \theta = 2 \sum_{p=2}^N \sum_{k=p}^N F_{D_{\perp}}^k l \cos \theta + \sum_{k=1}^N F_{D_{\perp}}^k l \cos \theta + \sum_{k=1}^N F_{D_{\parallel}}^k l \sin \theta, \quad (3.29)$$

$$2NmB \cos \varphi \sin \theta = 2 \sum_{p=2}^N \sum_{k=p}^N F_{D_{\parallel}}^k l \sin \theta + \sum_{k=1}^N F_{D_{\parallel}}^k l \sin \theta + \sum_{k=1}^N F_{D_{\perp}}^k l \cos \theta. \quad (3.30)$$

Comparing Eqs. (3.29) and (3.30) with Eqs. (3.25) and (3.26), we obtain the same results after the simplification. Summarizing all the possibilities of rod number N , all the $F_n^{(p+1)+}$, F_n^{p-} , $F_f^{(p+1)+}$, and F_f^{p-} terms are vanished, and we always obtain the same results of Eq. (3.17) and (3.18), which can be reorganized in an ODE system

$$\begin{cases} \dot{\theta} = -\left(\frac{3mB}{\varepsilon_{\parallel} l^3 N^2}\right) \frac{\cos \varphi}{\sin \theta} \\ \dot{\phi} = -\left(\frac{3mB}{\varepsilon_{\perp} l^3 N^2}\right) \frac{\sin \varphi}{\cos \theta} \end{cases}. \quad (3.31)$$

When Stokes flow passes a circular cylinder of small aspect ratio ($\gamma \leq 10$), like the rod in our experiment, the ratio of the hydrodynamic drag coefficients in its long axial direction and in its short axial direction is about 1,¹¹⁻¹² i.e., $\varepsilon_{\parallel} = \varepsilon_{\perp} = \varepsilon$. According to the geometrical relations in Fig. 3.7(b), the normalized length of the chain is approximately estimated to be $\lambda \approx \cos \theta$. Therefore, Eq. (3.31) is furtherly simplified as

$$\begin{cases} \dot{\lambda} = \frac{\cos \varphi}{\tau} \\ \dot{\varphi} = -\frac{\sin \varphi}{\tau \lambda} \end{cases}, \quad (3.32)$$

where $\tau = \frac{\varepsilon l^3 N^2}{3mB}$. Clearly, the extending and the rotating motions of the rod cluster are coupled together and both of their transient speeds depend on the same parameter τ . In order to solve the Eq. (3.32) analytically, we define a constant α as the reciprocal of τ and have

$$\begin{cases} \dot{\lambda} = \alpha \cos \varphi \\ \dot{\varphi} = -\frac{\alpha \sin \varphi}{\lambda}, \alpha = \frac{1}{\tau} \end{cases}. \quad (3.33)$$

Take the derivation with respect to time t for the first equation of Eq. (3.33)

$$\ddot{\lambda} = -\alpha \dot{\varphi} \sin \varphi. \quad (3.34)$$

Replace $\dot{\varphi}$ with its expression by the second equation in Eq. (3.33)

$$\ddot{\lambda} = \alpha^2 \frac{\sin^2 \varphi}{\lambda} \rightarrow \ddot{\lambda} \lambda = \alpha^2 \sin^2 \varphi. \quad (3.35)$$

From the expression of $\dot{\lambda}$ in Eq. (3.33), we also have

$$\dot{\lambda}^2 = \alpha^2 \cos^2 \varphi. \quad (3.36)$$

Sum Eqs. (3.35) and (3.36)

$$\ddot{\lambda} \lambda + \dot{\lambda}^2 = \alpha^2. \quad (3.37)$$

Take the derivation with respect to time t for the second equation of Eq. (3.33)

$$\ddot{\varphi} = -\alpha \left(\dot{\varphi} \cos \varphi - \dot{\lambda} \frac{\sin \varphi}{\lambda^2} \right). \quad (3.38)$$

Replace $\dot{\lambda}$ and $\dot{\varphi}$ with their expressions in Eq. (3.33)

$$\ddot{\varphi} = -\alpha \left(\frac{\dot{\varphi} \cos \varphi}{\lambda} - \frac{\dot{\lambda} \sin \varphi}{\lambda^2} \right) = 2\dot{\varphi}^2 \cot \varphi. \quad (3.39)$$

Now, we separate the variables of Eq. (3.33)

$$\begin{cases} \ddot{\lambda} \lambda + \dot{\lambda}^2 = \alpha^2 \\ \ddot{\varphi} = 2\dot{\varphi}^2 \cot \varphi \end{cases} \quad (3.40)$$

To solve the first equation of Eq. (3.40), let $\mu = \lambda^2$, we have

$$\begin{aligned} \dot{\mu} &= 2\lambda \dot{\lambda} \\ \ddot{\mu} &= 2\dot{\lambda} \dot{\lambda} + 2\lambda \ddot{\lambda} = 2(\dot{\lambda}^2 + \lambda \ddot{\lambda}) \end{aligned} \quad (3.41)$$

The first equation of Eq. (3.40) becomes

$$\ddot{\mu} = \frac{\alpha^2}{2}. \quad (3.42)$$

Solve Eq. (3.42)

$$\mu = \frac{\alpha^2}{4} t^2 + C_1 t + C_2. \quad (3.43)$$

Since λ is defined as $\cos \theta$, then $\mu \leq 1$. We have constrained conditions

$$\frac{\alpha^2}{4} t^2 + C_1 t + C_2 - 1 \leq 0. \quad (3.44)$$

However, $\frac{\alpha^2}{4}$ is definitely positive, so Eq. (3.44) cannot be satisfied by all t . λ can still be expressed as

$$\lambda = \pm \sqrt{\frac{\alpha^2}{4} t^2 + C_1 t + C_2}. \quad (3.45)$$

The solution with positive sign is selected for its physical meaning.

The constant C_2 can be determined by (3.45) at $t = 0$

$$\lambda(t=0) = \sqrt{C_2} \rightarrow C_2 = \lambda_0^2, \quad (3.46)$$

and constant C_1 can be determined by taking the first derivation of Eq.(3.45) with respect to t

$$\dot{\lambda}(t=0) = \frac{\frac{1}{2}\left(\frac{\alpha^2 t}{2} + C_1\right)}{\sqrt{\frac{\alpha^2 t^2}{4} + C_1 t + C_2}} \bigg|_{t=0} = \frac{C_1}{2\sqrt{C_2}}. \quad (3.47)$$

According to Eq. (3.33), we have

$$\dot{\lambda}(t=0) = \alpha \cos \varphi_0, \quad (3.48)$$

then,

$$\frac{C_1}{2\sqrt{C_2}} = \alpha \cos \varphi_0 \rightarrow C_1 = 2\alpha\lambda_0 \cos \varphi_0. \quad (3.49)$$

To solve the second equation of Eq. (3.40), we divide it by $\dot{\varphi}$

$$\frac{\ddot{\varphi}}{\dot{\varphi}} = 2\dot{\varphi} \cot \varphi. \quad (3.50)$$

The left side of Eq. (3.50) can be rewritten as

$$\frac{\ddot{\varphi}}{\dot{\varphi}} = \frac{d(\ln \dot{\varphi})}{dt}. \quad (3.51)$$

Combine Eqs. (3.50) and (3.51)

$$\frac{d(\ln \dot{\varphi})}{dt} = 2 \frac{d\varphi}{dt} \cot \varphi. \quad (3.52)$$

Multiply Eq. (3.52) with dt

$$d(\ln \dot{\varphi}) = 2 \cot \varphi d\varphi. \quad (3.53)$$

Rewrite Eq. (3.53) in integral form

$$\int_{\varphi_0}^{\varphi} d(\ln \dot{\varphi}) = \int_{\varphi_0}^{\varphi} 2 \cot \varphi d\varphi \rightarrow \ln \dot{\varphi} - \ln \dot{\varphi}_0 = 2(\ln(\sin \varphi) - \ln(\sin \varphi_0)). \quad (3.54)$$

Then, Eq. (3.54) becomes a new ODE

$$\ln \frac{\dot{\varphi}}{\dot{\varphi}_0} = \ln \left(\frac{\sin \varphi}{\sin \varphi_0} \right)^2 \rightarrow \dot{\varphi} = c \sin^2 \varphi, C = \frac{\dot{\varphi}_0}{\sin^2 \varphi_0}. \quad (3.55)$$

Separate variables of Eq. (3.55)

$$\dot{\varphi} = C \sin^2 \varphi \rightarrow \frac{d\varphi}{\sin^2 \varphi} = C dt. \quad (3.56)$$

Solve Eq. (3.56) by integrating its both sides

$$\int_{\varphi_0}^{\varphi} \frac{1}{\sin^2 \varphi} d\varphi = \int_0^t C dt \rightarrow \cot \varphi_0 - \cot \varphi = Ct. \quad (3.57)$$

Reorganize Eq. (3.57)

$$\varphi = \cot^{-1} (C_3 t + C_4), C_3 = -C = \frac{-\dot{\varphi}_0}{\sin^2 \varphi_0}, C_4 = \cot \varphi_0. \quad (3.58)$$

Plug the expression of $\dot{\varphi}$ in Eq. (3.33), we obtain C_3

$$C_3 = \frac{-\left(-\alpha \frac{\sin \varphi_0}{\lambda_0}\right)}{\sin^2 \varphi_0} = \frac{\alpha}{\lambda_0 \sin \varphi_0}. \quad (3.59)$$

Now, let's plug the expression of α into the coefficient C_1 , C_2 , C_3 and C_4 , and reorganize the solutions of in Eq. (3.32)

$$\begin{cases} \lambda(t) = \sqrt{\frac{1}{4} \left[\left(\frac{t}{\tau} \right) + c_1 \right]^2 + c_2}, \lambda(t) \leq 1 \\ \varphi(t) = \cot^{-1} \left[c_3 \left(\frac{t}{\tau} \right) + c_4 \right] \end{cases}, \quad (3.60)$$

where $c_1 = 4\lambda_0 \cos \varphi_0$, $c_2 = \lambda_0^2 - 4\lambda_0^2 \cos^2 \varphi_0$, $c_3 = \lambda_0^{-1} \csc \varphi_0$ and $c_4 = \cot \varphi_0$, and λ_0 and φ_0 are the initial values for the cluster. The parameter τ has an apparent physical meaning, and is similar to the retardation time constant in a typical viscoelastic problem. Equation (3.60)

is used to fit the data in Fig. 3.6(b), and both the blue and pink dash curves represent the best fittings for $\lambda(t)$ and $\varphi(t)$, respectively. The retardation time τ_λ extracted from the $\lambda(t)$ fitting is 30 ± 2 ms, and the retardation time τ_φ extracted from the $\varphi(t)$ fitting is 29 ± 2 ms, *i.e.*, $\tau_\lambda \approx \tau_\varphi$. Thus the theoretical prediction agrees with experimental data very well.

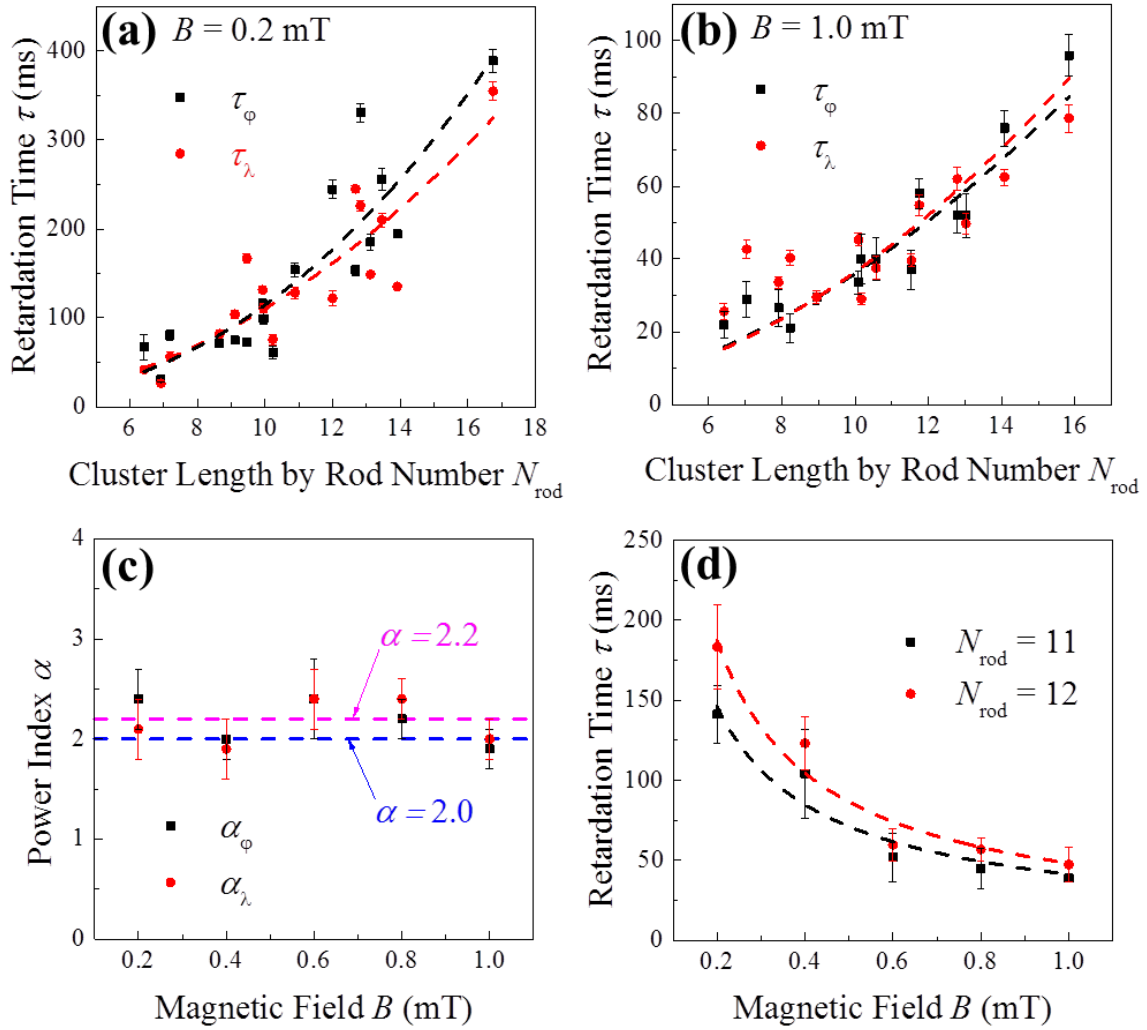


Figure 3.8 The plots of retardation time τ_λ (red circle) and τ_φ (black square) versus chain length N_{rod} at (a) $B = 0.2$ mT and (b) $B = 1.0$ mT. The dash curves are the fitting by a power law. (c) The plot of exponents α_λ (red circle) and α_φ (black square) for $B = 0.2, 0.4, 0.6, 0.8, 1.0$ mT. The average $\alpha = 2.2$ (pink dash line) is close to the theoretical prediction $\alpha =$

2 (blue dash line). (d) The plots of the average retardation time τ versus B for $N_{\text{rod}} = 11$ (black square) and 12 (red circle). The dash curves are the fittings *via* a power law.

According to our model, the retardation time τ is proportional to N^2 and inversely proportional to B . Figure 3.8(a) and (b) plot the τ_λ (red circle) and τ_ϕ (black square) extracted from different magnetic cluster with different length at $B = 0.2$ mT and 1.0 mT, respectively. Both figures show that τ_λ and τ_ϕ increases monotonically with $N_{\text{rod}} = L_s / l$. A power law relationship, $\tau(N) \sim N^\alpha$, is used to fit these data. For $B = 0.2$ mT, one obtains $\alpha_\lambda = 2.1 \pm 0.3$ (red dash curve) and $\alpha_\phi = 2.4 \pm 0.3$ (black dash curve); for $B = 1.0$ mT, $\alpha_\lambda = 2.0 \pm 0.2$ (red dash curve) and $\alpha_\phi = 1.9 \pm 0.2$ (black dash curve). Clearly the exponent α fluctuates around 2.0. In fact, experimentally we extract α_λ and α_ϕ for $B = 0.2, 0.4, 0.6, 0.8$ and 1.0 mT, and they are plotted against B in Fig. 3.8(c). Both α_λ (red circle) and α_ϕ (black square) remain constant and the statistical average of all exponent values (including α_λ and α_ϕ) is $\alpha = 2.2 \pm 0.2$ (pink dash line), which agrees well with the theoretical value, $\alpha = 2$ (blue dash line).

The relation of τ versus B is also plotted in Fig. 3.8(d). Here we select two groups of clusters with $N_{\text{rod}} = 11 \pm 0.5$ and $N_{\text{rod}} = 12 \pm 0.5$, and τ is the average value of the retardation time constants from both τ_λ and τ_ϕ . The τ decreases monotonically with B . By fitting the two data sets with a power law, $\tau(B) \sim B^\beta$, we obtain that $\beta = -0.8 \pm 0.1$, which is quite close to the theoretical expectation of $\beta = -1$. Thus, the model based on the *zig-zag* chain extension and rotation describes the dynamic extension of the magnetic cluster of FMRs very well.

3.4 Long-term Behavior of FMRCs under a Static B -field

Figure 3.9(a) illustrates the morphological transition of FMRCs' suspension ($C_R = 1 \text{ mg/mL}$) before ($t < 2 \text{ s}$) and after ($t > 2 \text{ s}$) the application of a static B field ($B = 5 \text{ mT}$), whose time scale ($\Delta t > 100 \text{ s}$) is much larger than the one of the immediate response of clusters to the B field ($\Delta t < 1 \text{ s}$). From the images, the clusters initially appear in black dots ($t = 0 \text{ s}$) and start to form linear chains in the B -field direction when it is applied ($t = 3 \text{ s}$). As the field is continuously applied, the chains become longer while the number of clusters becomes fewer ($t = 10$ and 100 s). This phenomenon suggests the clustering behavior among the extended FMRCs in their longitudinal directions.

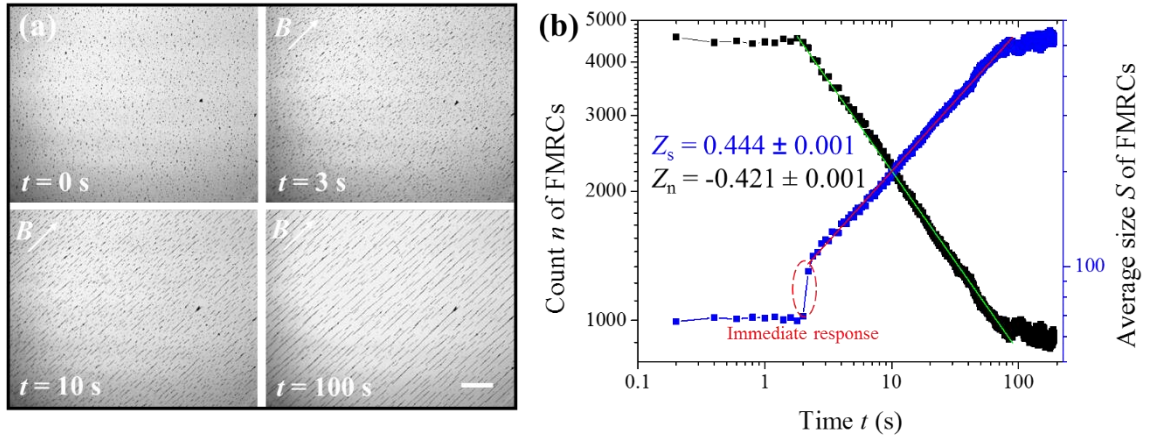


Figure 3.9 The clustering behavior of extended FMRCs in their longitudinal directions. (a) The represented images of FRMCs suspension at $t = 0, 3, 10$ and 100 s ; (b) Quantitative data of the clustering behavior fit by the power law with respect to the time t .

In order to quantitatively analyze the behavior of FMRCs, we define the total count of FMRCs in each image as n and the average size of FMRCs as S . Here, S equals to the average length of FRMCs L normalized by the average rod length l , i.e., $S = L/l$. The statistics of chain-like FRMCs extracted from the complete sequence (fps = 20) of Fig. 3.9(a) is shown in Fig. 3.9(b). From the log-log plots, one can see the average size $S(t)$ of

FMRCs (blue square) increases while the count of FMRCs $n(t)$ decreases (black square) along time t after the B -field is applied at $t = 2$ s. Therefore, the aggregation between FMRCs in their longitudinal directions are confirmed quantitatively. According to Eq. (1.15), the dynamic exponent Z can be calculated by the linear fits on the log-log curves of $S(t)$ and $n(t)$, which yields $Z_s = 0.444 \pm 0.001$ and $Z_n = 0.421 \pm 0.001$. Since Z_s and Z_n are very close and both of them fall into the region of Z , *e.g.*, $0.3 \sim 1.5$, the clustering behavior of FMRCs also follows the power law very well.¹⁰¹ Interestingly, there is jump of $S(t)$ just after the B -field is applied ($2 \text{ s} < t < 3 \text{ s}$) while $n(t)$ maintains constantly. This is caused by the self-extension behavior of the FMRCs in Section 3.2.

According to Eq. (1.15), the average chain length L is also a function of the particle volume fraction Φ and the magnetic number σ , which are directly corresponding to the rod

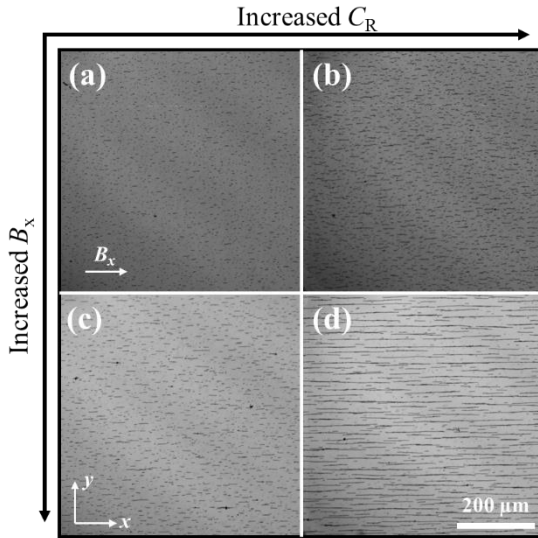


Figure 3.10 Representative images of FMRCs induced by B_x . (a) $C_R = 0.1 \text{ mg/mL}$, $B_x = 1 \text{ mT}$; (b) $C_R = 0.5 \text{ mg/mL}$, $B_x = 1 \text{ mT}$; (c) $C_R = 0.1 \text{ mg/mL}$, $B_x = 25 \text{ mT}$; (d) $C_R = 0.5 \text{ mg/mL}$, $B_x = 25 \text{ mT}$.

concentration C_R and the magnetic field B_x in our experiments. Therefore, we fix the application time of B -field to be 150 second, and tune the resulted rod structures by changing C_R and B_x . As shown in Fig. 3.10, the chain-like FMRCs start to form stripy patterns as C_R and B increase. In order to study these patterns, we define D as the average distance between the chains in the y direction. Figure 3.10(a) and (b) compares

the resulted structures in the suspension of $C_R = 0.1 \text{ mg/mL}$ and $C_R = 0.5 \text{ mg/mL}$ when $B_x = 1 \text{ mT}$. The chains are longer in the x direction (larger L) and more compacted in the y

direction (smaller D) for higher concentration C_R . Figure 3.10(c) and (d) show the structures in the suspension of $C_R = 0.1$ mg/mL and $C_R = 0.5$ mg/mL when $B_x = 25$ mT. Clearly, density of the chain structures can be tuned up by increasing either C_R or B_x .

In order to systematically study the effect of C_R and B_x , we vary the rod concentration from 0.1 mg/mL to 1.0 mg/mL, and the magnetic field B_x from 1 to 25 mT. The resulted L and D are plotted in Fig. 3.11(a) and (c). From the log-log plots in Fig. 3.11(a), the average chain length L increases with the rod concentration C_R , and for the same C_R , L value increases with B_x . According to Eq. (1.15) we have a log-log relation as for a fixed t

$$L \propto t_B^{-Z} \rightarrow L \propto (\Phi\sigma)^Z \rightarrow \ln L = a_L \ln C_R + b_L \ln B_x, \quad (3.61)$$

where a_L and b_L are constants independent of C_R and B_x . By a linear fit, one can obtain the value of a_L from the slope and $b_L \ln B_x$ from the interception, as shown in Fig. 3.11(a). Fig. 3.11(b) depicts a_L and $b_L \ln B_x$ versus B_x . a_L increases with B_x , which implies its dependence on B_x , with a mean value of $a_L = 0.8 \pm 0.5$. Applying a linear fit on the linear-ln plot of $b_L \ln B_x$ with respect to B_x , b_L is 0.34 ± 0.04 .

From the log-log plots of in Fig. 3.11(c), the average transverse distance of chains D decreases with the rod concentration C_R , and for the same C_R the D value decreases by B_x . We expect a similar relations of Eq. (3.61) on D

$$\ln D = a_D \ln C_R + b_D \ln B_x, \quad (3.62)$$

where a_D and $b_D \ln B_x$ are constants independent of C_R and B_x . By a linear fit of the log-log plot, a_D and b_D are obtained and plotted versus B_x in Fig. 3.11(d). a_L maintains the same value at $B_x = 1, 5$ mT and increases at $B_x = 25$ mT. The average value of $a_L = -0.98 \pm 0.08$. From the linear fit of $b_D \ln B_x$ with respect to $\ln B_x$, we obtain $b_D = -0.090 \pm 0.002$.

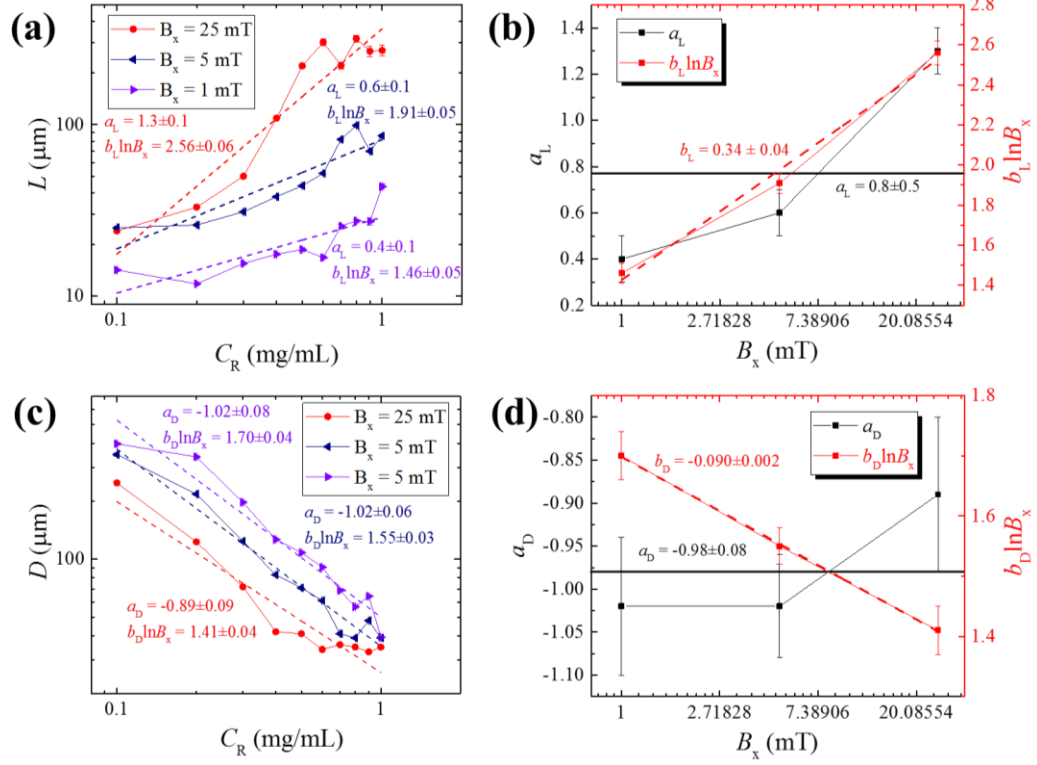


Figure 3.11 The statistic results of rod concentration dependent structural parameters of FMRCs under different B_x field. (a) The average chain length L versus C_R ; (b) The a_L and $b_L \ln B_x$ versus B_x ; (c) The average chain distance D versus C_R ; (d) a_D and $b_D \ln B_x$ versus B_x . All dash lines are linear fit results and the solid lines indicate the mean values.

3.5 Conclusions

In this chapter, we studied the dynamic process of FMRCs under an external magnetic field. This process can be divided into two parts in time domain. After the application of the external field, the FMRCs are extended and aligned in the B -field direction, forming magnetic chains. Then, these small chains gradually aggregate in their longitudinal direction and eventually form a stripy pattern. Under our experimental conditions, the first time domain is less than 1 second and the second time domain is as long as 100 seconds. The first dynamic process is treated as an immediate response of

FMRCs to an external B -field, while the second one is considered as a long-term response of FMRCs to the same B -field.

The immediate response of the FMRCs to the external field is essential an extension-rotation coupled motion in the B -field direction. The origins of this coupled motion come from the field-driven alignment of both FMRs and FMRCs, accompanied with the rearrangement of FMRCs from the side-by-side raft-like structure to the end-to-end chain-like structure. A theoretical model based on a *zig-zag* chain was developed to analytically characterize the motion. A retardation time constant τ extracted from dynamics of FMRCs is inversely proportional to B -field, and is a square function of the chain length N , which is consistent with the theoretical prediction. It is expected that this model can be adapted for the dynamics of magnetic clusters consisted of other anisotropic magnetic particles, as well as magneto-elastic behavior of other soft matters consisting of FMRCs.

Unlike the immediate response, the long-term response of FMRCs comes from the magnetic interaction between FMRCs rather than the self-excitation of individual clusters. Due to the magnetic interaction under B -field, the chain-like FMRCs aggregate in their longitudinal direction to form longer chains. More importantly, it leads to a morphological change of the rod suspensions. The resulted stripy patterns can be characterized by the average chain length L and their transvers distance D . A systematic study on L and D shows that they can be tuned by the rod concentration C_R and the magnetic field B_x . Scaled by a power law (Eqs. (3.61) and (3.62)), the coefficients a and b associated with C_R and B_x are both positive for L while being negative for D . Therefore, the average chain length L increases with C_R or B_x , and the average transverse distance D decreases with C_R or B_x .

CHAPTER 4

FERROMAGNETIC-ROD CLUSTER UNDER A CHANGING MAGNETIC FIELD

Towards to our eventual goal of applying magnetic powered clusters on the stroke treatment, we investigate the behavior of FMRCs under a magnetic field with changing directions in this chapter. In the last chapter, we introduced the immediate and long-term responses of FMRCs to a static B -field. As a result, a stripy pattern of long chains formed in the suspension, whose structural parameters L and D can be tuned by the rod concentration C_R and magnetic field B . However, if the applied B -field changes its direction as a function of time, the formed chain structure would also change. In this chapter, we first introduce the setup of a magnetic field system to generate changing fields. We then discuss the dynamic behavior of the formed chains under a suddenly applied field B_y in their transverse direction. A network-like structure can be formed based on the initial structural parameter L/D and the applied field B_y . We also discuss the size of FMRCs under a rotational B -field. Lastly, we introduce the dynamics of FMRCs under a rotational magnetic field.

4.1 Setup of Magnetic Field System

To experimentally manipulate the FMRCs under a changing magnetic field, we need to develop a control system to generate specific field patterns. We have the choices

of two types of field sources, permanent magnets and electromagnets. To maintain a static and strong magnetic field, permanent magnets have the advantages of being low-cost and auxiliary-free. They are easy to operate and do not generate heat during operation. These advantages may outweigh its drawback in applications where low-cost and simple operation is preferred. However, a dynamic magnetic field with tunable patterns and fast switching is needed in our study, which necessitates the use of electromagnet coils. Theoretically, the magnetic field induced by a solenoid can be simulated using Bio-Savart law.¹⁰²⁻¹⁰³ The *Biot-Savart* law describes the magnetic field $\vec{B}$ at position $\vec{r}$ in the free space generated by a wire C with electrical current I ,

$$\vec{B}(\vec{r}) = \frac{\mu_0}{4\pi} \int_C \frac{Id\vec{l} \times (\vec{r} - \vec{l})}{|\vec{r} - \vec{l}|^3} \quad (4.1)$$

where $\vec{l}$ is the position vector of an elementary segment of wire and the current vector in it is $Id\vec{l}$. The pointing vector from the elementary current $Id\vec{l}$ to $\vec{B}$ is $\vec{r} - \vec{l}$. From Eq. (4.1), the magnetic field $\vec{B}$ is contributed by all the current elements over the wire C . When the wire is wrapped onto a cylindrical core of magnetic permeability μ , it becomes a coil and the distribution of its induced magnetic field $\vec{B}$ can be calculated according to Eq. (4.1) and expressed in Cartesian coordinates

$$\vec{B}(x, y, z) = \frac{\mu n I R}{4\pi} \int_0^L \int_0^{2\pi} \frac{\hat{i}(x-X)\cos\theta + \hat{j}(x-X)\sin\theta + \hat{k}(R-y\sin\theta - z\cos\theta)}{\left[(z-R\cos\theta)^2 + (y-R\sin\theta)^2 + (x-X)^2\right]^{3/2}} d\theta dX. \quad (4.2)$$

R and L are the radius and length of the coil, n is the number of turns per unit length of the coil (Fig. 4.1(a)). From the simulated single air-core ($\mu = \mu_0$) solenoid (Air-core Solenoid

#14825, Science Source, Waldoboro, ME) with current $I = 1$ A, the generated magnetic field is calculated by Matlab (The MathWorks, Natick, MA) and predicted to rapidly decrease below 1 mT outside the coil, as shown in Fig. 4.1(b).

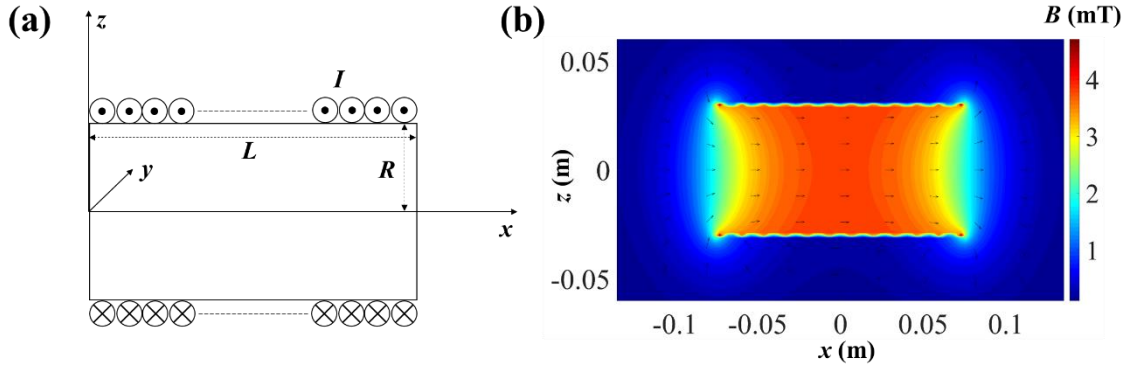


Figure 4.1 The numerical calculation on a coil induced B field (a) the modeling description and (b) the simulating results.

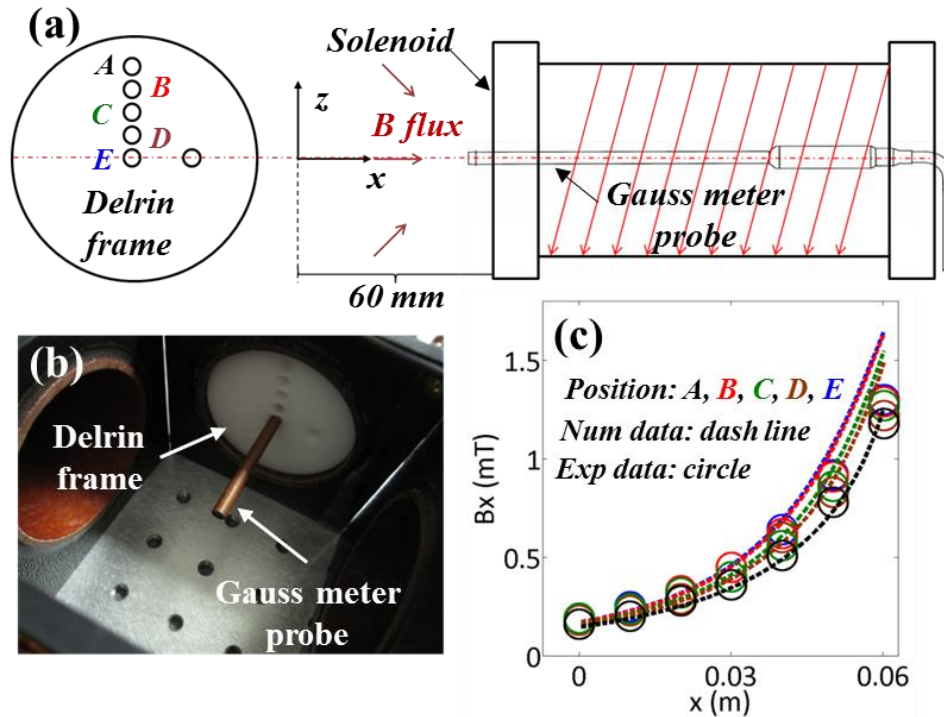


Figure 4.2 The calibration of the magnetic field induced by a single solenoid (a) the scheming locations for data collection of B_x ; (b) the prototype of the Delrin frame in the measuring setup; (c) the theoretical prediction (dash line) compared with the experimental results (circle).

To verify the theoretical calculation, the field strength was measured. As shown in Fig. 4.2(a) and (b), a Gauss meter (Model 5080, F. W. BELL) probe through a homemade delrin frame embedded in a solenoid was used to measure the magnetic field component B_x along x axis at different z locations (through A , B , C , D and E holes). According to the plots in Fig. 4.2(c), the theoretical prediction was consistent with the experimental data.

We used two pairs of electric coils to generate a changing magnetic field. Figure 4.3(a) illustrates the setup of such devices. Two pairs of solenoids are placed orthogonally and connected to two power supplies and controlled by a computer. In each pair, the coils are connected in series to generate the required magnetic field in the same direction. To generate a rotating magnetic field, two alternating currents (AC) were used in the coil pairs. They have the same magnitude and frequency, but a phase lag of $\pi/2$. Figure 4.3(b) shows the magnetic field distribution within a $4R \times 4R$ blue-dash frame at different phase angles in one revolution. We can see the direction of the field rotates in x - y plane and the field magnitude is relatively uniform in the center.

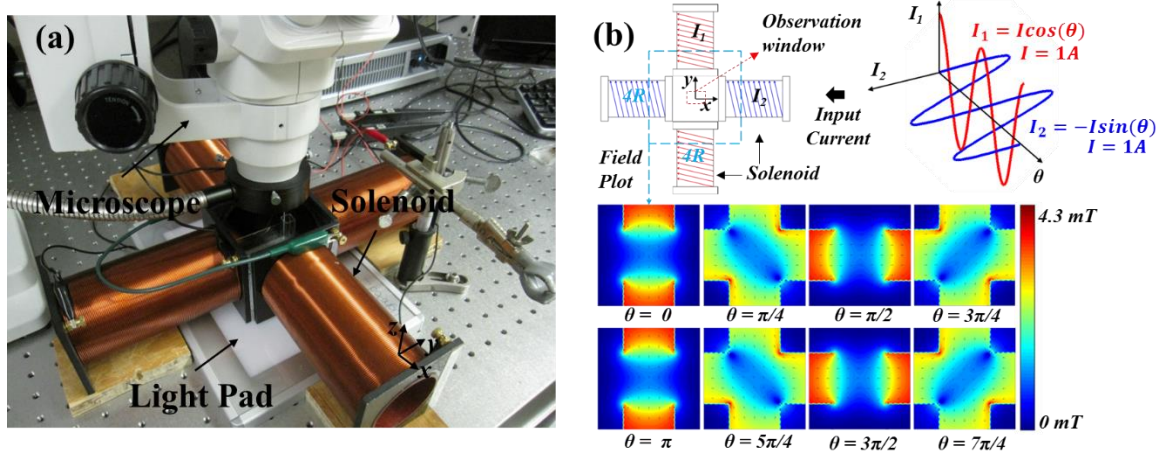


Figure 4.3 The rotational magnetic field generated by (a) two orthogonal pairs of coils and visualized by (b) the simulation of the field distribution in one period.

To study the FMRC, both the magnetic field strength B and the rotational frequency f need be tunable. However, this range is limited by the inductance of the coils. Figure 4.4 plots the peak-to-peak value of B field versus the peak-to-peak value of the input AC. B field linearly increases with the input current. Maximum peak-to-peak B decreases with frequency f . We chose our magnetic field condition with B and f values falling in the red dashed box, with $B_{\max} < 20$ mT and $f_{\max} < 75$ Hz.

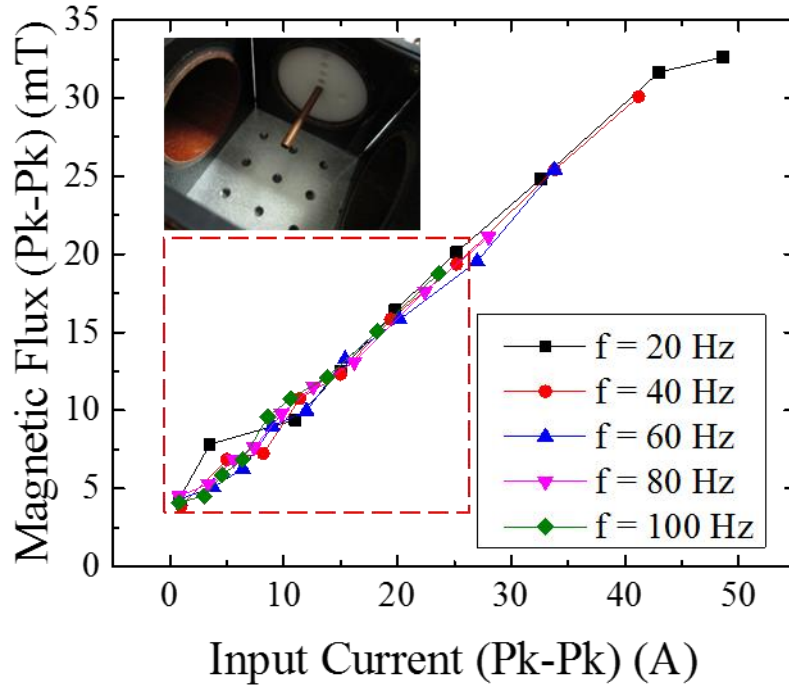


Figure 4.4 Calibration results of the dynamic field generating system. The B -field strength and frequency can be continuously tuned within the range of the red dash frame.

4.2 Formation of FMRs' Network under a Changing Magnetic field

Initial chain network

Figure. 4.5 shows a sequence of images at every 50 ms to represent the dynamic behavior of FMRCs ($C_R = 0.5$ mg/mL) under a changing B field. At $t = 0$ s, long chain structure formed after the application of $B_x = 25$ mT for 150s. From $t = 0$ s to $t = 0.05$ s, B_x was turned off and $B_y = 5$ mT was turned on. We can see the ends of the chains bent towards

y direction. As B_y was continuously applied ($t \geq 0.1$ s), the length of the bending parts increased while the entire chains rotated in the same direction. As a result, long chains were connected to form FMRs' network, and short chains aligned in the y direction. Interestingly, closed loops of chains were formed at $t = 0.2$ s and 0.25 s.

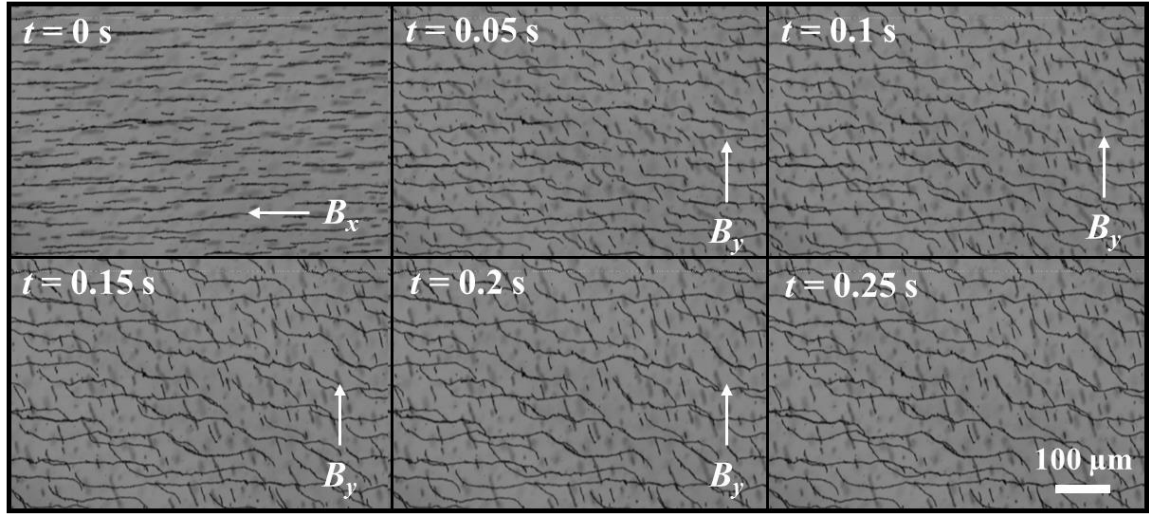


Figure 4.5 Dynamic behavior of FMRCs under B -field with a suddenly changed from x direction to y direction. The magnetic chains are bent and rotated by B_y .

The same transverse magnetic field ($B_y = 5\text{mT}$) were repeatedly applied on the rod suspensions with different initial chain structures to obtain different networks. As we recall from last Chapter, the chain structures can be tuned by C_R and B_x to obtain different L and D . For further simplification, we now use a dimensionless number L/D to represent the features of the initial chain structure. We also define an area fraction ϕ , the ratio of cellular area to the total area of the image, to characterize the resulted structures. ϕ will be a function of time t during the dynamic process. Figure. 4.6(a) shows such a curve $\phi(t)$ and a sequence of representative images of the rod suspensions ($C_R = 0.5$ mg/mL). The frame at $t = 1$ s shows the initial morphology of the FMRCs, of which $L/D = 5.4 \pm 0.2$. Every closed loop is identified and filled with different colors by a custom-made image

processing routine. After that ($t > 1$ s), $B_y = 5$ mT was applied, the cellular area increased ($t = 1.5, 1.75, 2$ s) rapidly until they formed a stable network structure. Saturated value of ϕ was around 58%.

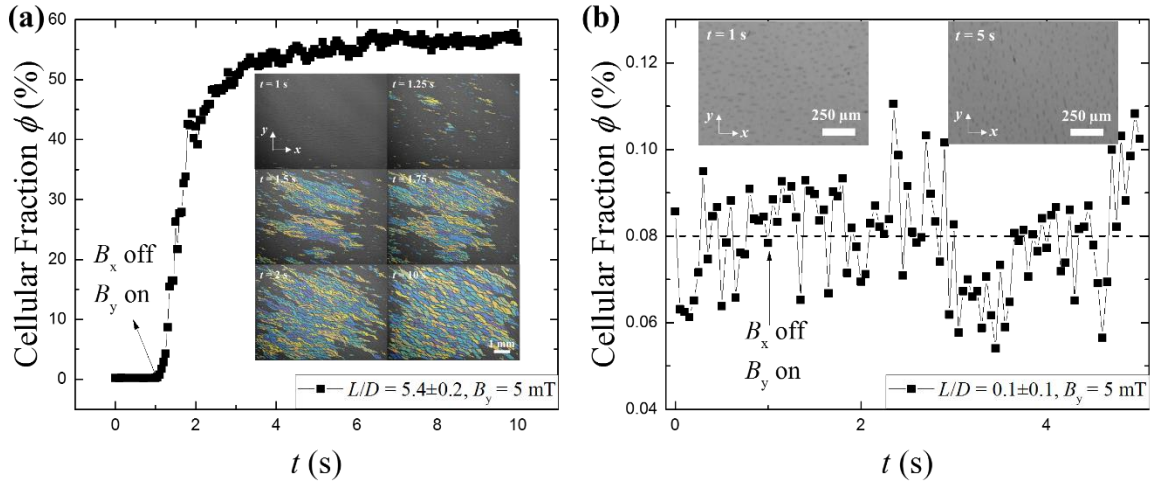


Figure 4.6 Dynamic transition of the of FMRCs induced by $B_y = 5$ mT (a) Image sequence and quantitative plot of cellular fraction ϕ versus time t when $C_R = 0.5$ mg/mL and $L/D = 5.4$. (b) Image sequence and quantitative plot of cellular fraction ϕ versus time t when $C_R = 0.1$ mg/mL and $L/D = 0.1$.

When the initial chain structure was diluted, *i.e.*, small average chain length L and large transverse distance D , a different structure showed up at the same B_y . As shown in Fig. 4.6(b), at $t = 1$ s the initial chain structure ($C_R = 0.1$ mg/mL) has $L/D = 0.1 \pm 0.1$. After the application of $B_y = 5$ mT ($t > 1$ s), all the short chains flipped 90° by B_y without any cellular formation. Transvers gap between chains was much larger than their length, there was no connections between them. This was confirmed by $\phi(t)$, whose value fluctuated around 0.08%.

There is a critical condition to form FMRs' network regarding the initial chain structures. In order to find this condition analytically, we illustrate the change of chain structures before and after the application of B_y in Fig. 4.7 (a) and (b). Initially, the chains

form and align themselves in x direction, resulting a stripy structure of parameters L and D . As shown in Fig. 4.5, the chains bend and rotate after the application of B_y .

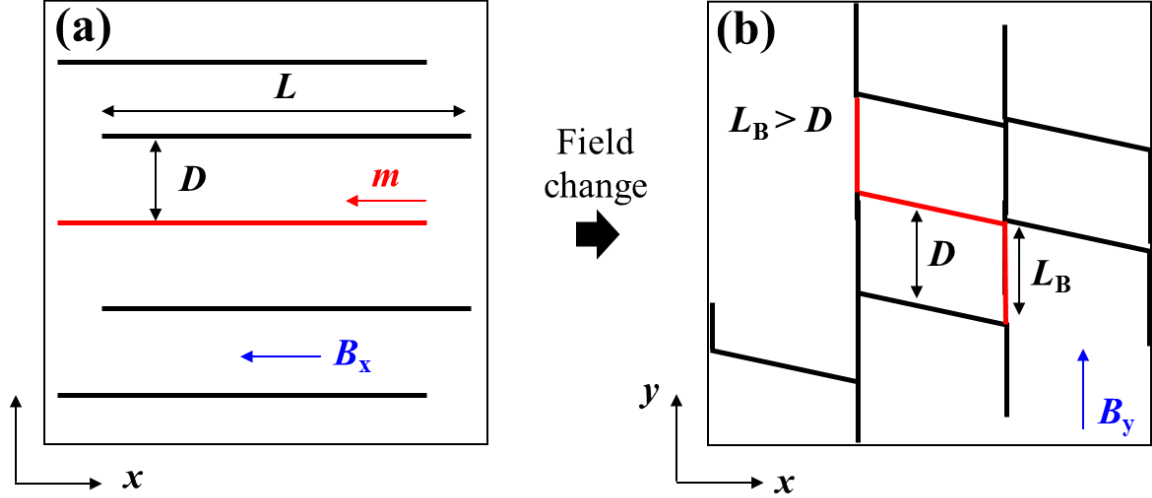


Figure 4.7 The analytical scheme on the structural change of FMRCs under a transverse magnetic field. (a) The initial structures of parameters L and D ; (b) The geometrical relations of L_B and D to form a closed loop.

For simplification, we assume the mass and magnetic moment is uniformly distributed along the chain length. Therefore, all the chains bend asymmetrically with a bending length L_B , and rotate locally around its center-of-mass. From Fig. 4.7(b), one can see the eventual bending length L_B has to be larger than the initial transverse distance D , in order to form a closed loop. However, L_B is limited by the chain length and its maximum value is $L/2$ when the chain bent entirely. Therefore, L_B is confined as $D \leq L_B \leq L/2$, which leads to the critical condition for network regarding L and D ,

$$\frac{L}{D} \geq 2 \quad (4.3)$$

This condition only depends on the initial structure of FMRCs, which can be experimentally confirmed. As shown in Fig. 4.8, the saturated cellular fraction ϕ_s is plotted

as a function of initial parameter L/D . ϕ_s is around zero when $L/D < 2$. Once $L/D > 2$, ϕ_s jumps to 30%. As L/D continues increasing, ϕ_s eventually settles around 50%.

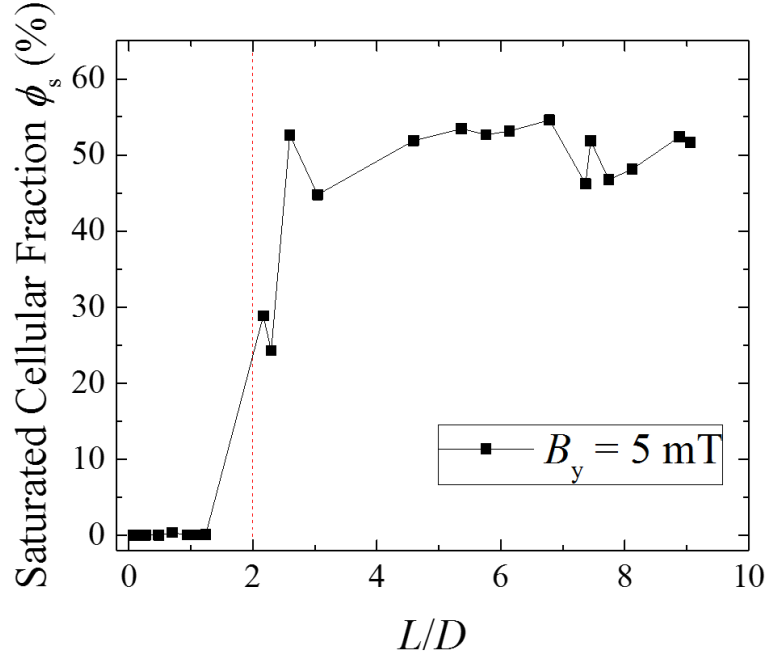


Figure 4.8 The resulted cellular fraction ϕ_s versus initial parameter L/D by $B_y = 5$ mT. The critical condition $L/D = 2$ is marked by a red dash line.

B_y dependent network

The effect of B_y to the formation of the network is studied in this section. In order to isolate the other factors from B_y , the initial structures were induced by the same $B_x = 25$ mT and $C_R = 0.3$ mg/mL with resulted value of L/D around 3.2. As shown in Fig. 4.9, the network structures in (a), (b) and (c) was separately induced by $B_y = 5, 15, 25$ mT. From the images, one can see the cellular area decreases with B_y . Figure 4.9(d) shows ϕ_s as a function of B_y , which was consistent to the observation.

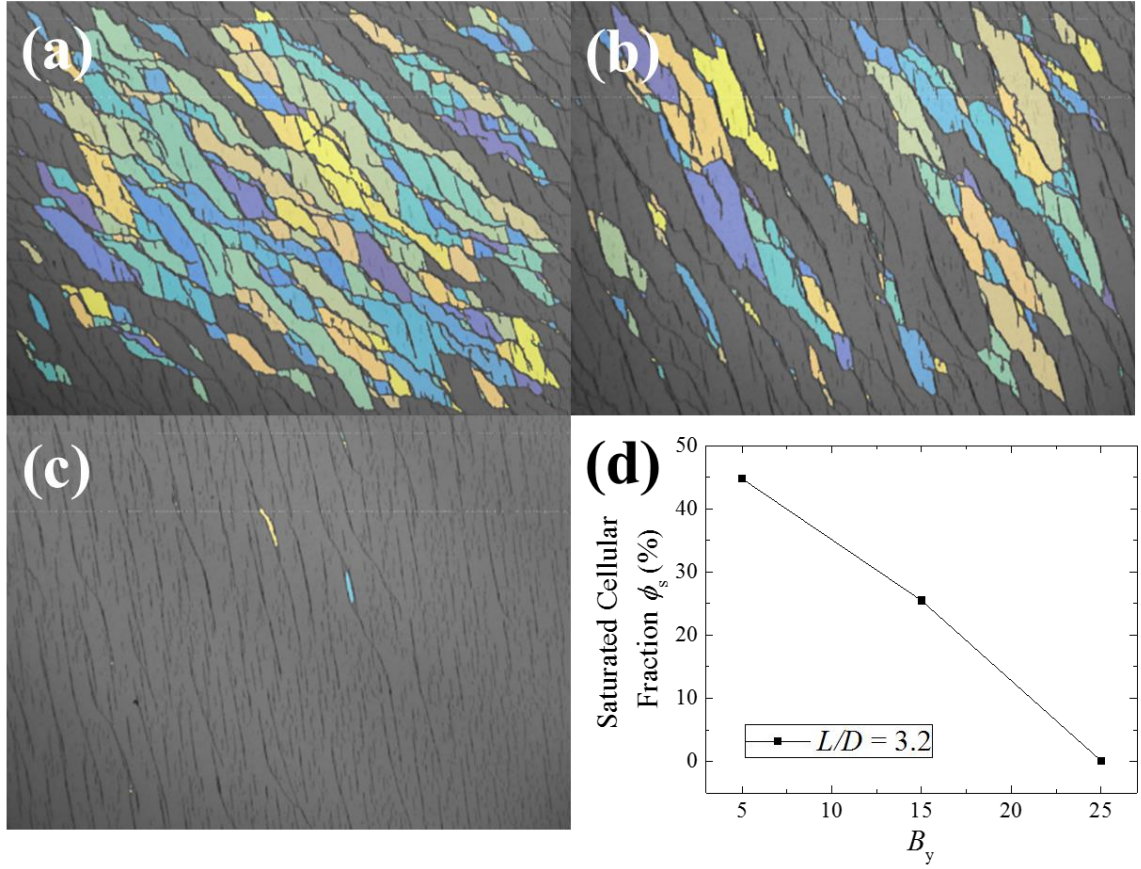


Figure 4.9 The network structures from the same initial conditions induced by different (a) $B_y = 5$ mT, (b) $B_y = 15$ mT and (c) $B_y = 25$ mT, of which saturated cellular fraction ϕ_s is plotted against B_y in (d).

To understand B_y effect on the network structures, we focus on the dynamic behavior of the chains. As shown in Fig. 4.10(a), a single magnetic chain bends and rotates with B_y . For simplification, we assume this occurs at the very moment of B_y application, so that B_y is still perpendicular to the chain. First, let's consider the entire chain rotates around its center-of-mass o with an initial angular velocity Ω_1 . According to Eq. (1.5), the magnetic field induced torque on the whole chain is $\Gamma_B = B_y m_L L$, where m_L is the magnetic moment per unit chain length. The hydrodynamic torque on it can be expressed by Eq.

(1.8), $\Gamma_B = \varepsilon_{\perp} \Omega_1 L^3 / 12$. According to the torque balance on the chain in a low Reynolds number fluid, we obtain the angular velocity Ω_1

$$\Omega_1 = \frac{12m_L B_y}{\varepsilon_{\perp} L^2}. \quad (4.4)$$

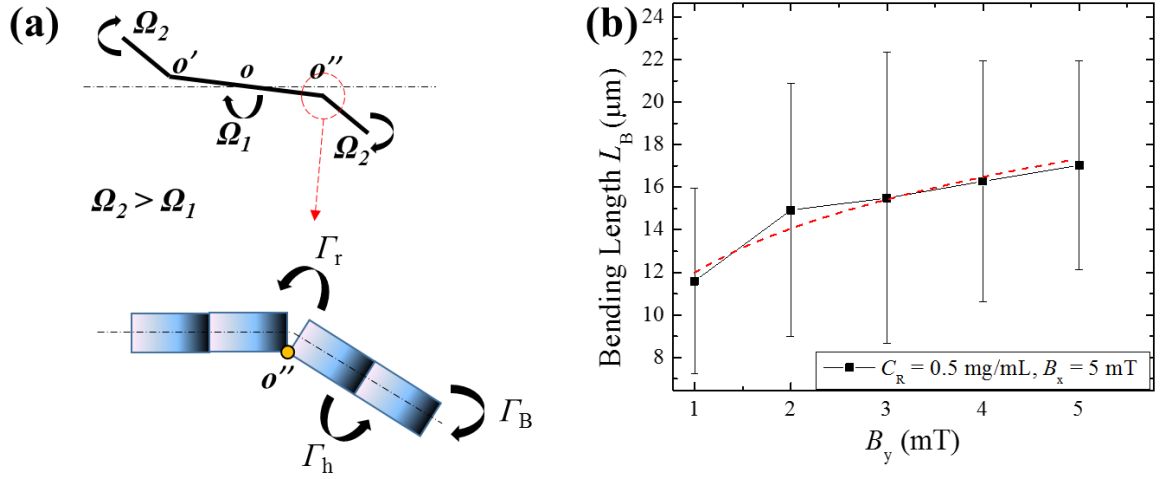


Figure 4.10 The B_y dependent bending length L_B (a) Theoretical model with torque analysis; (b) Experimental data confirms the increase of L_B by B_y . The dash curve is the fitting result.

There is a bending part of length L_B at the ends of the chain. It has a different angular velocity Ω_2 around the bending point o' (or o'') from the chain. We obtain the magnetic torque $\Gamma_B = B_y m_L L_B$ and the hydrodynamic torque $\Gamma_h = \varepsilon_{\perp} \Omega_2 L_B^3 / 3$, respectively. Besides these two torques, there is an additional torque by the magnetic attraction between the rods at the bending point o' (or o''), as shown in the enlarged part of Fig. 4.10(a). This torque is always against the bending direction of the chain and restoring bent part back to the chain. Therefore, it is named as a restoring magnetic torque Γ_r , whose expression will be derived later. Here, we just use its expression in Eq. (4.9), and have $\Gamma_r = \frac{3\mu_0 m_L^2 d}{4\pi l^2}$,

where l and d are the average length and diameter of individual rods. Applying the torque balance $\Gamma_B = \Gamma_r + \Gamma_h$, we obtain the angular velocity Ω_2 ,

$$\Omega_2 = \frac{3B_y m_L}{\varepsilon_{\perp} L_B^2} - \frac{9\mu_0 m_L^2 d}{4\pi \varepsilon_{\perp} l^2 L_B^3} \quad (4.5)$$

From our theoretical model shown in Fig. 4.10(a) and the experimental observation, the bending behavior of the chain occurs only if $\Omega_2 > \Omega_1$. Plugging the expression of Eqs. (4.4) and (4.5), the bending length L_B has to satisfy

$$\left(\frac{2L_B}{L} \right)^2 < 1 - \frac{3\mu_0 m_L d}{4\pi l^2 L_B B_y}. \quad (4.6)$$

According to Eq. (4.6), the maximum value of L_B increases with B and decrease with m . When B is infinite, $L_B = L/2$ and the chain bends entirely by the B field. When m is large enough and the right side value of Eq. (4.5) is negative, L_B can never satisfy Eq. (4.5). Figure 4.10(b) shows the average bending length L_B in the suspension ($C_R = 0.5$ mg/mL) by different B_y . It confirms our theoretical prediction that L_B increases with B_y . The experimental data can be well fitted by Eq. (4.6) (red dash curve).

Now let's consider how B_y affects the resulted network structure through L_B . As shown in Fig. 4.11(a) and (b), a closed loop is formed in the rectangular shape, of which area can be estimated as $A \approx D(L-2L_B)$. When L_B increases with B_y , it is possible to form a closed loop by satisfying $L_B > D$. However, the area of the loop actually decreases by L_B , because D is determined initially and the unbent length $L-2L_B$ decreases. As shown in Fig. 4.11(c), the loop becomes smaller while the overlapped length of the bending parts from different chains increases. An extreme situation is two chains of the same length are bent entirely and synchronously, so that there is no sweeping area overlapped during this process, leading to no network of the chains.

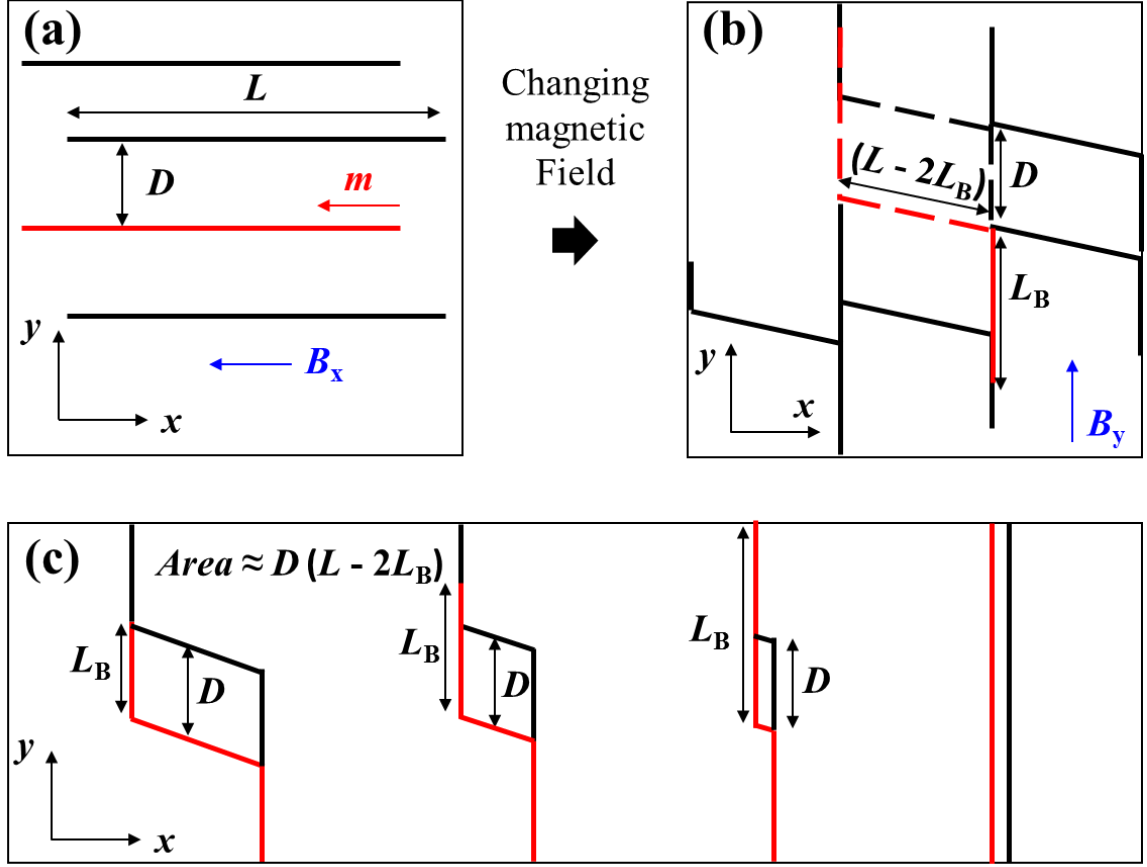


Figure 4.11 The network structure changed by B_y through the bending length L_B . (a) The initial chain structures, (b) The resulted network structures, (c) The area of a close loop induced by different L_B .

A more comprehensive study on the B_y dependent network was carried out with the parameter L/D . For each batch of the experiments, the same B_y was used to induce the network structure from the initial chain structure of different L/D . The resulted ϕ_s against L/D is plotted in Fig. 4.12(a). For all the curves, ϕ_s is below 1% when $L/D < 2$, which confirms the critical condition of Eq. (4.3) regardless of B_y . As L/D continuously increases, ϕ_s curves of different B_y start to increase and reach to a stable value around 50% eventually. Therefore, $\phi_s(L/D)$ curve is essentially shifted in the horizontal direction by B_y . If we define the a transition parameter $(L/D)_{\text{tran}}$ associated with $\phi_s = 5\%$, we can find this value

and its error bar using a linear fit between the data points across $\phi_s = 5\%$ in Fig. 4.12(a). As a result, $(L/D)_{\text{tran}}$ is plotted against B_y in Fig. 4.12(b). $(L/D)_{\text{tran}}$ monotonously increases with B_y . It is interesting to learn that the structural transition of FMRCs is induced by B_y , but also suppressed by B_y when it is too large.

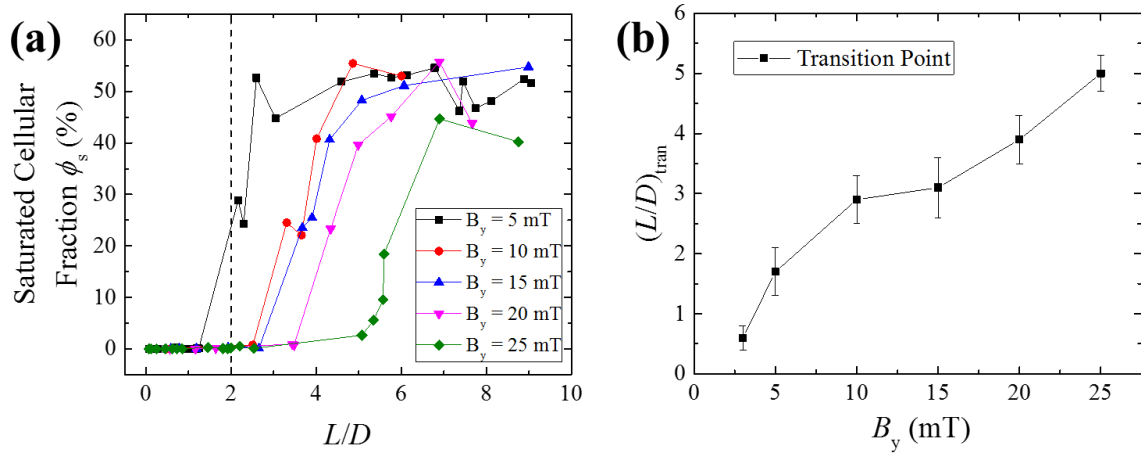


Figure 4.12 The structural transition of FMRCs manipulated by different B_y (a) $\phi_s(L/D)$ curves under different B_y ; (b) The transition parameter $(L/D)_{\text{tran}}$ versus B_y .

4.3 Equilibrium Size of FMRCs under a Rotational Magnetic field

Here, we present a systematic study on the equilibrium morphology of FMRCs under a rotational magnetic field.

Theoretical consideration

When the FMRs' suspension ($C_R = 4$ mg/mL) is subjected to a rotational magnetic field ($B = 6$ mT), the chain-like clusters are driven to follow the field. Figure 4.13(a) shows the different morphologies of the rotating chains when the rotational frequency of the B -field $f = 5, 10, 15, 20$ Hz. From the images, the size of the FMRCs decreases while the number of the FMRCs increases with f , which implies the long chains are broken to short ones. Figure 4.12(b) plots the average length of the FMRCs L versus the field frequency f .

The experimental data is fit by a power function $L = bf^a$. From the fitting results, the power index $a = -0.73 \pm 0.02$.

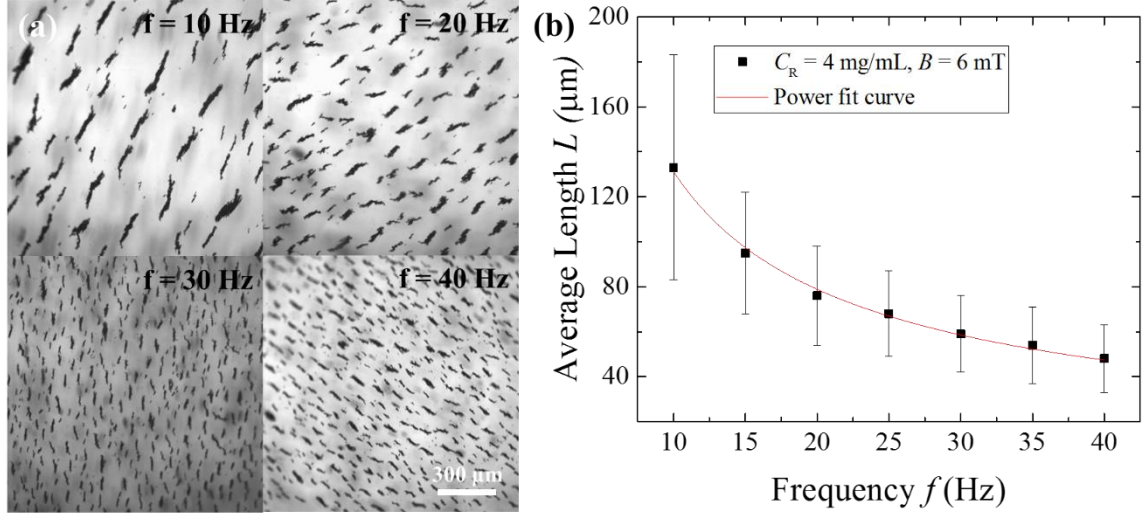


Figure 4.13 Morphology of FMRCs suspension ($C_R = 4$ mg/mL) subjected to a rotational magnetic field ($B = 6$ mT) with different frequency of $f = 10, 15, 20, 25, 30, 35$ and 40 Hz. (a) Images of FMRCs at different f ; (b) Statistic results (sample number > 50) of the average chain length N versus f .

We already know the size of magnetic chains of paramagnetic beads under a rotational magnetic field is determined by the competition between the magnetic torque and the hydrodynamic torque. The chain length is proportional to the square root of Mason number, *i.e.*, $N \sim \frac{B}{\sqrt{f}}$. However, the chain-like FMRC is stiffer than the chain-like PMBC due to the magnetic interaction between rods, and the isotropic volume exclusion. To estimate the maximum length of FMRCs under rotational magnetic field, one only need consider the stability of the outside rod. When a FMRC rotates at a frequency of f , the tangential velocity along the its length is $v_\theta(x) = 2\pi fx$, where x is the distance to the center of the FMRC. The hydrodynamic drag force and torque on the outside (or right in Fig. 4.14) rod is,

$$\begin{aligned}
F_h^{FMR} &= \int_{x=(N/2-1)l}^{Nl/2} \varepsilon_{\perp} v_{\theta}(x) dx = \pi \varepsilon_{\perp} f l^2 (N-1) \\
\Gamma_h^{FMR} &= \int_{x=(N/2-1)l}^{Nl/2} \varepsilon_{\perp} v_{\theta}(x) x dx = 2\pi \varepsilon_{\perp} f l^3 \left(\frac{N^2}{4} - \frac{N}{2} + \frac{1}{3} \right)
\end{aligned} \tag{4.7}$$

Figure 4.14(a) illustrates the force analysis on the right-end rod. Forces are balanced in the horizontal and the vertical directions. In the horizontal direction, F_r is magnetic attracting force between FMRs and F_N is the counteracting normal force. Combining the dipole concentrated model (Section 3.1) and Eq. (1.11), we have $F_r = -\frac{3\mu_0 m^2}{2\pi l^4}$ and $F_{\theta} = 0$. Since the force decays with 4th order of dipolar distance, we only consider the magnetic interaction of adjacent rods. The negative sign of F_r means the rods are attracted in the axial direction, and the zero value of F_{θ} means there is no transverse force component between rods. In the vertical direction, there is a hydrodynamic force F_h (Eq. 4.7), which is balance by the frictional force νF_r , where ν is the frictional coefficient between the ends of two adjacent rods. Plugging in the force expressions, we have the force based limitation of the chain length

$$N < \frac{3\nu\mu_0 M^2}{8\varepsilon_{\perp} f \gamma^4} + 1, \tag{4.8}$$

where M is the volume magnetization of the rod and the rod aspect ratio $\gamma = l/d$.

Figure 4.14(b) and (c) illustrates the torque balance on the rod in two situations. Comparing with the PMBC model, there is an additional torque Γ_r induced by F_r to prevent the rod from rotating round in either direction (yellow circles at the rod corner). Therefore, Γ_r is treated as a restoring torque with an expression of,

$$\Gamma_r = F_r \frac{d}{2} = -\frac{3\mu_0 m^2 d}{4\pi l^4} \tag{4.9}$$

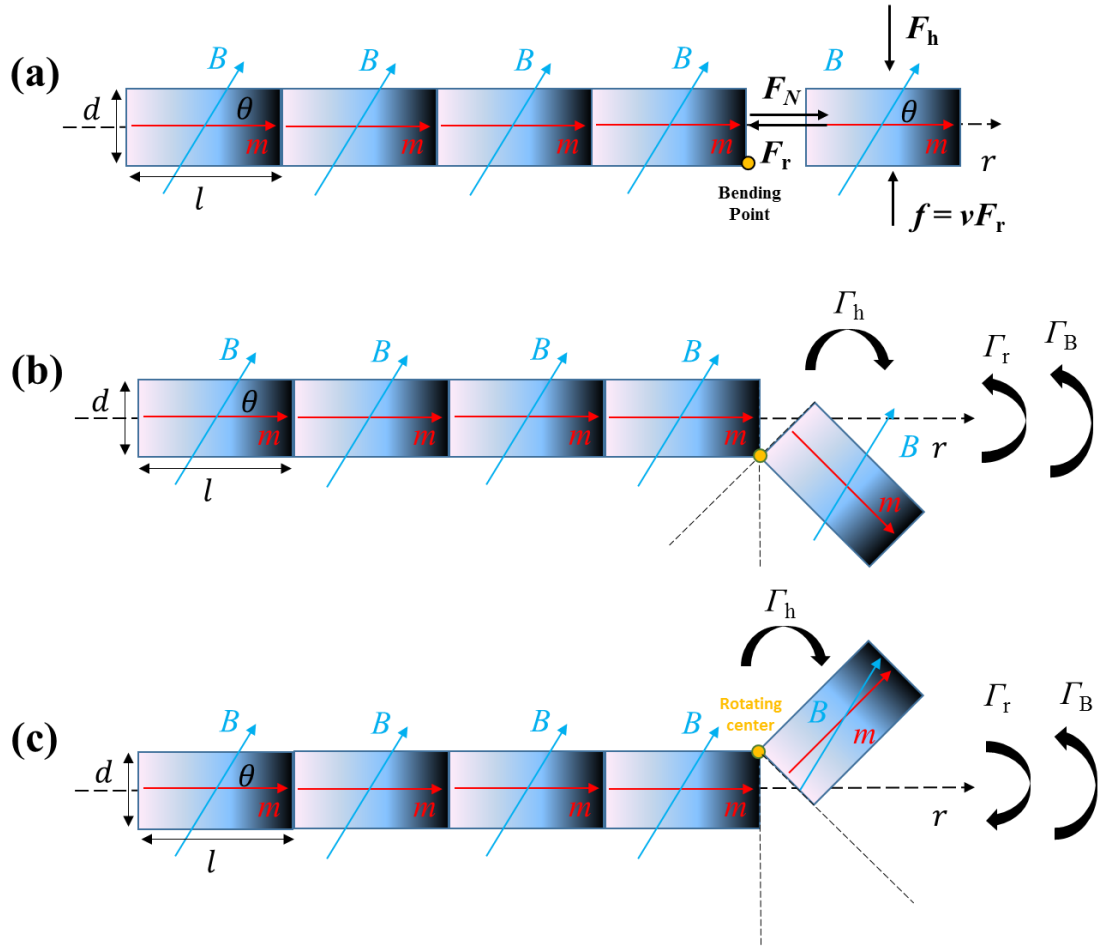


Figure 4.14 Force and torque analysis on the rightmost FMR in the chain (a) the force balance on the rod (b) the torque balance on the rod when it rotates in clockwise direction and (c) the torque balance on the rod when it rotates in counter-clockwise direction.

However, the magnetic torque Γ_m^{FMR} and the hydrodynamic drag torque Γ_h^{FMR} may cause the rod to fold in the opposite directions, as shown in Fig. 4.14(b) and (c). When $\Gamma_h^{FMR} \geq \Gamma_r + \Gamma_m^{FMR}$, the rod is dominated by the hydrodynamic torque with a clockwise rotation. When $\Gamma_m^{FMR} \geq \Gamma_r + \Gamma_h^{FMR}$, the rod is dominated by the magnetic torque with a counter-clockwise rotation. Combining both conditions, the torque limited chain length is given by,

$$Mn_1 - Mn_2 \leq \left(\frac{N^2}{4} - \frac{N}{2} + \frac{1}{3} \right) \leq Mn_1 + Mn_2 \quad (4.10)$$

where $Mn_1 = \frac{MB \sin \beta}{8\epsilon\eta f \gamma^2}$, $Mn_2 = \frac{3\mu_0 M^2}{128\epsilon\eta f \gamma^5}$. Similar to the Mason number Mn (Eq. (1.18)), Mn_1 represents the competition of the rod-field magnetic interaction against the rod-fluid hydrodynamic interaction. However, there is an additional item Mn_2 representing the rod-rod magnetic interaction over the rod-fluid hydrodynamic interaction. Since both Mn_1 and Mn_2 are inversely proportional to the high order of the rod aspect ratio γ , particularly for $Mn_2 \sim \gamma^{-5}$, one can conclude that the FMRCs of short rods can survive with a much larger length variation under the same B -field conditions. If FMRs are linearly magnetized by the B field, i.e., $M \sim B$, and N is large, one can still obtain the relation of the field dependent chain size from Eq. (4.9)

$$N \sim Bf^{-1/2}, \quad (4.11)$$

Combing the force restriction of Eq. (4.8), the power index a of the relation $N \sim f^{-a}$ should be in the range from 0.5 to 1, which is consistent to the fitting results of in Fig. 4.13(b).

Fabrication of FMRs with different aspect ratios

According to Eq. (4.10), the boundaries of FMRCs' length is sensitive to the rod aspect ratio γ . To study the rod dependent length of FMRCs, we fabricated nickel rods of different sizes by an oblique angle deposition (OAD) method.⁶⁴ OAD is a physical vapor deposition technique in which the substrate is normally positioned at a large angle with respect to deposition vapor direction. As shown in Fig. 4.15(a), in order to fabricate uniform Nickel nanorods on the substrate, a 500 nm diameter polystyrene bead monolayer was formed on Si substrate using convective self-assembly method.¹⁰⁴ The bead-coated

substrates were loaded into a custom built electron beam evaporation chamber. Nickel (Ni, 99.95%, Alfa Aesar, Ward Hill, MA) was deposited at a vapor incident angle of 86° and at a rate of ~ 0.5 nm/s, monitored by a quartz crystal microbalance (QCM) facing directly toward the incident vapor. Ni nanorods of length ~ 1 μm were obtained when the QCM reading reached 2 μm , as shown in Fig. 4.15(b) and (c).

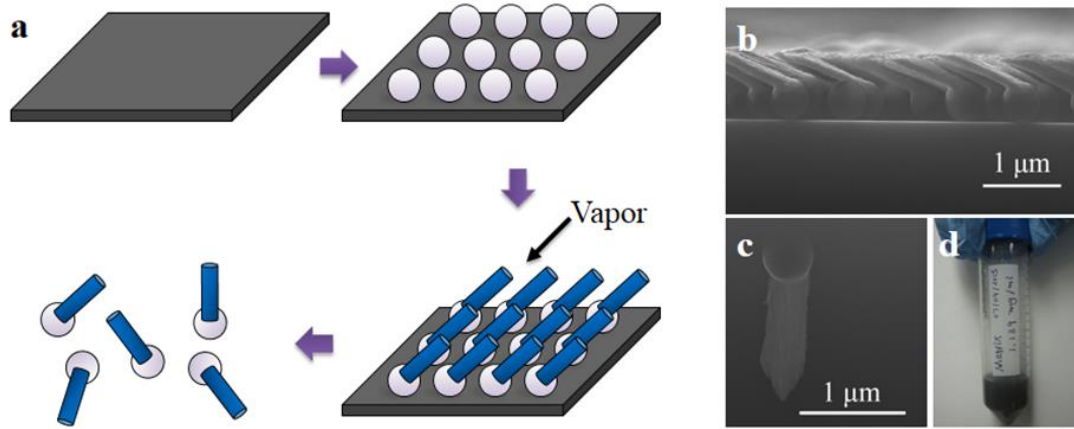


Figure 4.15. Nickel rods fabrication process using OAD and convective self-assembly methods. (a) Schematic process of fabrication indicated in clockwise direction: self-assembled monolayer of polystyrene beads on a cleaned silicon wafer; uniform nickel rods grown on beads using OAD method; rods washed into suspension of PVP; (b) Side view of nanorods on silicon substrate; (c) A single nanorod with a polystyrene bead; (d) Rods suspended in PVP (MW = 40K Da) solution, forming a matrix of known concentration.

To obtain a stable suspension of FMRs, the Ni rods on substrates were dipped in PVP (Polyvinylpyrrolidone, MW = 360K Da, Sigma-Aldrich, St. Louis, MO) solution (w/w = 10%) for 24 hours. Then the substrates were sonicated for 1 minute in another PVP (MW = 40K Da, Sigma-Aldrich, St. Louis, MO) solution (w/w = 10%) for 30 sec. During the sonication, most of the rods were released from the substrates and suspended in PVP solution to form a stable matrix as shown in Fig. 4.15 (d). The final concentration of the nanorods was determined by the weight difference of substrates before and after the sonication. Before each experiment, the rods in matrix were extracted by a strong

permanent magnet, washed by water for 2-3 times and sonicated in Tetrahydrofuran (THF) solution for 30-45 seconds to dissolve the polystyrene beads.

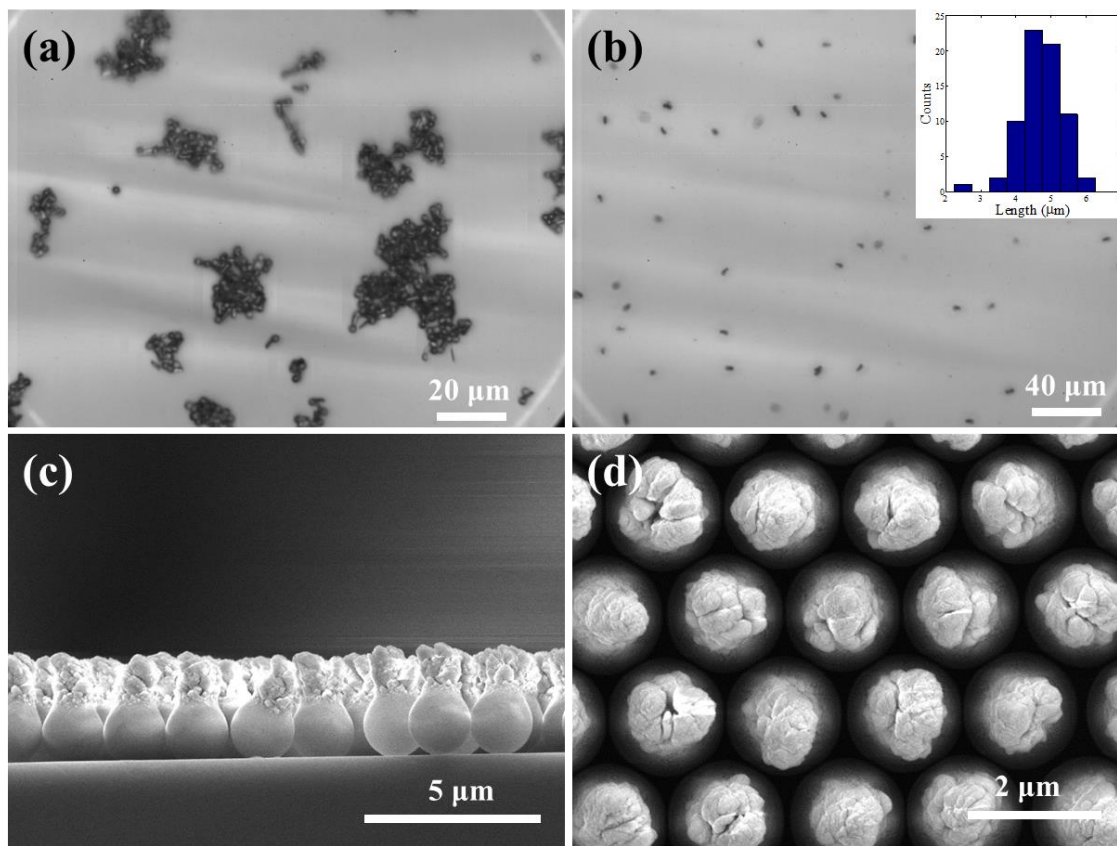


Figure 4.16 The 3 μm nickel rods under optical microscopes (a) aggregated in water, (b) suspended in PVP solution with a normal size distribution; and the 2 μm nickel rods under SEM (c) side view on the substrate and (d) top view on the substrate.

Figure 4.16(a) and (b) also shows 3 μm rods with bead heads aggregated in water and suspended in PVP solution. The size distribution of the rods (including the bead head) is insert on the right-up corner in Fig. 4.16(b). As a result, the dimension of the 3 μm rod is $l = 2.78 \pm 0.59 \mu\text{m}$, $d = 1.90 \pm 0.06 \mu\text{m}$ and $\gamma \approx 1.47$. Figure 4.16(c) and (d) shows the scanning electron microscope (SEM) images of 2 μm rods with beads on the substrate. From the images, the dimension of the 3 μm rod is $l = 1.88 \pm 0.08 \mu\text{m}$, $d = 1.78 \pm 0.06 \mu\text{m}$ and $\gamma \approx 1.05$.

Rod dependent length of FMRCs

Since the rod has different dimensions and mass, we fix the rod number concentration as 5×10^6 /mL in the experiments. Figure 4.17(a) and (b) depicts the average length L of the FMRCs formed by 3 μm (as shown in Fig. 4.16 (a) and (b)) and 2 μm FMRs (as shown in Fig. 4.16 (c) and (d)) at different B and f . For both rods, L increases with B and decreases with f , which confirms the theoretical prediction of Eq. (4.10).

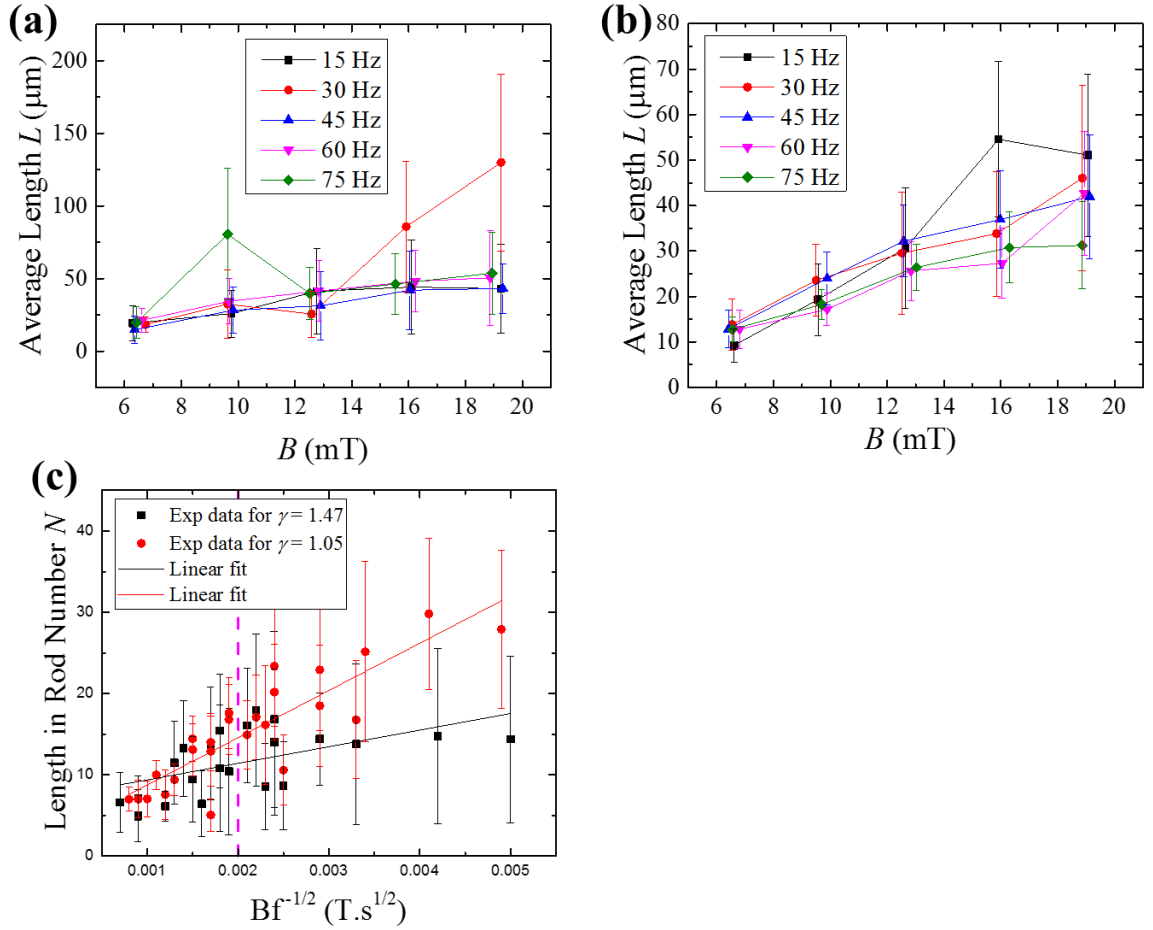


Figure 4.17 Average size of FMRCs formed by (a) 3 μm FMRs and (b) 2 μm FMRs at different B and f , and (c) Average chain length normalized by rod length, *i.e.*, rod number N versus field parameter $Bf^{-0.5}$.

According to Eq. (4.10), the rod number N under different field conditions is proportional to $Bf^{-0.5}$. Figure 4.17(c) adapts all the data points in Fig. 4.17(a) and (b) in the relation of

$N \sim Bf^{-0.5}$. From the results, there is no obvious increasing trend of N for both 3 μm FMRCs (black square) and 2 μm FMRCs (red dot) when $Bf^{-0.5} < 0.002 \text{ T}\cdot\text{s}^{0.5}$, while the increasing trend becomes prominent when $Bf^{-0.5} > 0.002 \text{ T}\cdot\text{s}^{0.5}$. Figure 4.17(c) also shows the linear fit curve for 3 μm FMRCs (black solid line) and 2 μm FMRCs (red solid line). The average number of 2 μm FMRs in a FMRC increases faster than the one of 3 μm FMRCs by $Bf^{-0.5}$. Considering the aspect ratio of 3 μm FMRs ($\gamma \approx 1.47$) and of 2 μm FMRs ($\gamma \approx 1.05$), the result is consistent with our theoretical prediction.

4.4 Combination of FMRCs under a Rotating Magnetic Field

As we observed in the previous experiments (Fig. 4.13(a)), there were always some short FMRCs rotating in the magnetic field with unsaturated length. Therefore, it is possible for two rotating FMRCs to combine into a larger FMRC.

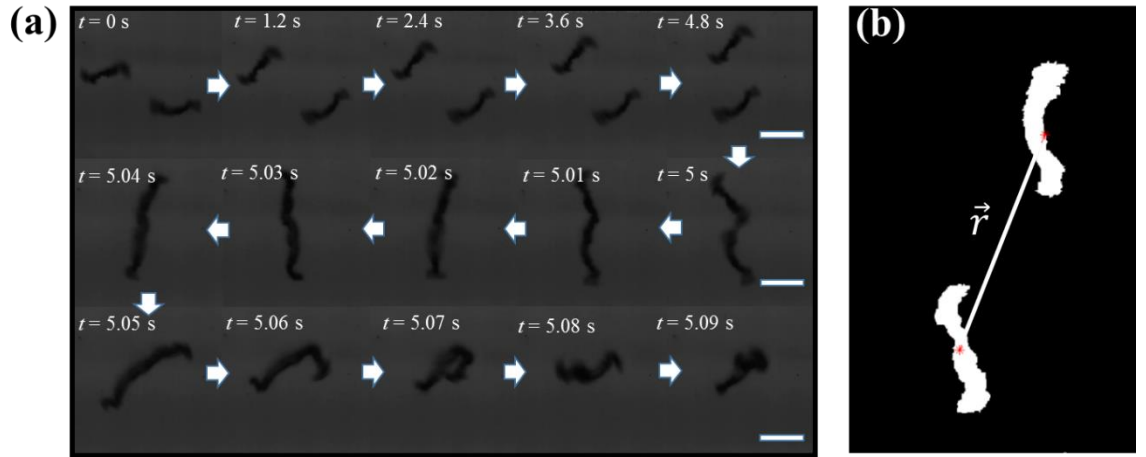


Figure 4.18 Combination process of two FMRCs (a) The image sequence before and after the osculation and (b) The center-to center vector $\vec{r}$ used to characterize the combination of the two FMRCs. The white scale bar in the top panel of (a) is 10 μm and in the middle and bottom panel is 20 μm .

Figure 4.18(a) shows such a dynamic process of the combination between two FMRCs driven by the magnetic field of $B = 5 \text{ mT}$ and $f = 20 \text{ Hz}$. From top panel of the frame

sequence, the FMRCs follow the B -field stably and approach to each other gradually. The middle and bottom panel show the image sequence within 0.1 second just after the two rods osculate. They stick together to form a longer FMRC. After several twists of the body the chain end starts to roll which has been predicted by our theoretical model as shown in Fig. 4.18(b). Eventually, it becomes a shorter and thicker FMRC to follow the rotational magnetic field.

To quantitatively describe the combination process, we defined a center-to-center vector $\vec{r}$ between the two FMRCs. Using a custom-made routine, the centroids of two FMRCs were extracted and marked with “*”. Therefore, the magnitude and the orientation of $\vec{r}$ can be extracted from the image sequence and plotted as a function of time $r(t)$ and $\theta(t)$. As seen in Fig 4.15(a) and (b), both $r(t)$ and $\theta(t)$ show an oscillation behavior, and their overall trend is to decrease with time t . This oscillation is caused by the periodically changed magnetic interaction between two synchronous-rotation FMRCs induced by the external B field. A fast Fourier Translation (FFT) of $r(t)$ and $\theta(t)$ (the inset figures in both Fig. 4.19(a) and (b)) shows that the spectral peaks for both $r(t)$ and $\theta(t)$ are located at $f = 20$ Hz, which is the f of the rotational magnetic field.

Such a joining process can be numerically simulated. Eq. (1.11) is adapted to account for the magnetic force between the two FMRCs with radial component F_r^{FMRC} and tangential component F_θ^{FMRC}

$$\begin{aligned} F_r^{FMRC}(t) &= \frac{3\mu_0 m^2}{4\pi r^4(t)} (3\cos^2 \alpha(t) - 1) \\ F_\theta^{FMRC}(t) &= \frac{3\mu_0 m^2}{4\pi r^4(t)} \sin 2\alpha(t) \end{aligned}, \quad (4.12)$$

where $\alpha(t) = \varphi(t) - \theta(t)$, and $\varphi(t)$ is the orientation of the magnetic moment m of FMRCs. Here, we assume the two FMRCs have the same orientation $\varphi(t)$ for their close size. Since the magnetic moment m is in the long axial direction of FMRC while the FMRCs closely follow the B field, $\varphi(t)$ can be expressed as $2\pi ft + \varphi_0$. Besides magnetic forces, there is a contacting repulsive force F_c^{FMRC} induced by the volume exclusion between two FMRCs and dominates their motions. Such a contact repulsive force between two magnetic particles at low Reynolds number has been well studied,¹⁰⁵ and used for dynamic simulation for magnetic beads under a rotating magnetic field.¹⁰⁶ Here, we assume the effective excluded volume of a rotational FMRC of length L equals to that of a spherical bead of diameter L . When $f = 20$ Hz, $L = 30$ μm , the Reynolds number is still as low as $Re = 0.06$. Then, F_c^{FMRC} can be adapted from the previous result¹⁰⁶

$$F_c^{FMRC}(t) = \alpha \frac{3\mu_0 m^2}{4\pi r^4(t)} e^{-\beta \left(\frac{r(t)}{L} - 1\right)}, r(t) \geq L, \quad (4.13)$$

where $\alpha = 2$ and $\beta = 10$ are empirical values, and F_c^{FMRC} is always in the radial direction. Similarly, we assume that the hydrodynamic drag coefficient of a rotating FMRC equal to the one on a spherical bead of diameter of L , and the hydrodynamic force on the FMRC can be expressed in both the radial and tangential directions as

$$\begin{aligned} \vec{F}_{hr}^{FMRC}(t) &= 3\pi L \eta \dot{r}(t) \\ \vec{F}_{h\theta}^{FMRC}(t) &= 3\pi L \eta r \dot{\theta}(t) \end{aligned} \quad (4.14)$$

Then, the governing equation of $\vec{r}$ at the low Reynolds number fluid can be set as

$$\begin{aligned} \vec{F}_c^{FMRC}(t) + \vec{F}_r^{FMRC}(t) + \vec{F}_{hr}^{FMRC}(t) &= 0 \\ \vec{F}_\theta^{FMRC}(t) + \vec{F}_{h\theta}^{FMRC}(t) &= 0 \end{aligned}, \quad (4.15)$$

Combining Eqs. (4.12)-(4.15), we have the following coupled differential equations with respect to $\vec{r}(t)$

$$\begin{aligned} 3\pi L\eta \frac{dr(t)}{dt} &= \frac{3\mu_0 m^2}{4\pi r^4(t)} \left[3\cos^2(2\pi ft + \varphi_0 - \theta(t)) - 1 \right] + \frac{3\mu_0 m^2}{2\pi l^4} e^{[-10(R(t)/l-1)]} \\ 3\pi L\eta \frac{r(t)d\theta(t)}{dt} &= \frac{3\mu_0 m^2}{4\pi r^4(t)} \sin(4\pi ft + 2\varphi_0 - 2\theta(t)) \end{aligned} \quad , (4.16)$$

These equations can be solved by ODE45 (Matlab, Mathworks) and the numerical results of $\vec{r}$ are shown in Fig. 4.19 as solid curves.

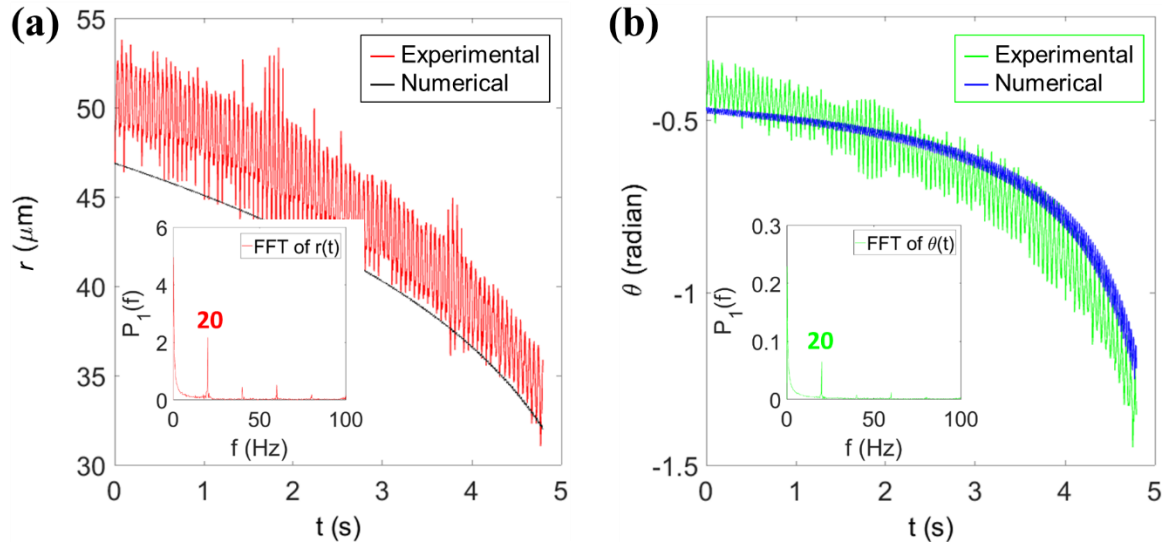


Figure 4.19 Experimental and numerical results of FMRCs mating process described by their center-to-center vector in (a) the magnitude $r(t)$ and (b) the orientation $\theta(t)$. The insert figures are the FFT results of experimental $r(t)$ and $\theta(t)$.

From numerical results of $r(t)$, the curve (black solid line) declines along the lower boundary of the oscillating experimental data (red curve) with a similar overall trend. However, the amplitude of the oscillation of simulated $r(t)$ is much smaller than the experimental data. This discrepancy may be caused by the strong variation of F_c^{FMRC} due to the anisotropic volume exclusion of FMRCs, which is not considered in our numerical model. The curve of simulated $\theta(t)$ (blue solid line) also shows a comparable overall trend

to the experimental data (green solid line). From the numerical and the experimental results, one can also see the oscillating amplitude of $\theta(t)$ gradually increases along time. This is caused by the stronger force interaction between two FMRCs and more impact from tangential motion of FMRCs to $\theta(t)$ when $r(t)$ decreases.

4.5 Conclusions

In this chapter, we have considered the dynamic behaviors of FMRCs under a suddenly and continuously changing magnetic field. Under a suddenly applied magnetic field in the transverse direction B_y , a transition from chain-like structures to network-like structures can be induced depending on a critical parameter (L/D) of the initial chain structure. Furthermore, the threshold value of this critical parameter for the structural transition can be changed by B_y . The resulted network structures can be used for the magnetic actuated filters, fabrication of smart materials and the reconstruction of the bio-tissues. When the FMRs suspension is submitted to a rotational magnetic field, the size of the FMRCs is confined by the field parameters and the aspect ratio of the FMRs. The theoretical part is based on the balance of the three torques induced by rod-field interaction, rod-rod interaction and rod-liquid interactions.

CHAPTER 5

FERROMAGNETIC-ROD CLUSTER ENHANCED THROMBOLYSIS

In the Chapter 1, we stated that the dose control and the effectiveness promotion of t-PA for thrombolysis are important to alleviate serious side effects such as hemorrhage in stroke treatments. In the last chapter, we studied some interesting behavior of FMRCs under a rotational magnetic field, which is partially owed to their strong interactions with the carrier liquid. Meanwhile, the hydrodynamic effect induced by the rotating FMRCs can greatly increase the mass transport of molecules, small proteins at the vicinity. This enhancement can be potentially employed to increase the mass transport of t-PA molecules at the blood clot interface for local ischemic stroke therapy. Dose control and effectiveness promotion can be potentially achieved while the risk of the stroke treatment is reduced. In this chapter, we first consider the theoretical model of molecular diffusion enhanced by the convection of rotating FMRs and demonstrate the effect in theoretical approaches. An analytical model is proposed based on the diffusion-limited theory on t-PA thrombolysis. The validity and efficiency of this enhanced treatment are demonstrated in PDMS channels. Finally, the thrombolytic rate is studied by considering the clustering effect of FMRs.

5.1 Theoretical Consideration

Self-diffusion of a molecule is considered as a thermal motion of a particle, whose process can be simulated by random walks. For a two dimensional (2D) random walk of a

particle starting from the origin of a in a Cartesian system at $t = 0$ the diffusivity D can be statistically estimated as,¹⁰⁷

$$D = \frac{\overline{x^2 + y^2}}{4t} \quad (5.1)$$

where (x, y) is the instant position of the particle at time t in one random-walk test and $\overline{x^2 + y^2}$ is the average value of the accomplished distance at time t by the multiple random-walk tests. In order to estimate the diffusivity by simulation, we assume the step size of each random walk is a constant h , with an arbitrary direction θ_n ($0 < \theta_n < 2\pi$). Therefore, the particle position after n steps can be expressed as,

$$\begin{cases} x_n = x_{n-1} + h \cos \theta_n \\ y_n = y_{n-1} + h \sin \theta_n \end{cases}, n = 1, 2, 3, \dots \quad (5.2)$$

Since we already know $(x_0, y_0) = (0, 0)$, the trajectory of a molecule with n -step random walks can be simulated and the h dependent diffusivity D can be estimated by the statistic average of the distance over the time t from N trials of random walks.

Now let's consider the hydrodynamic effect and add it to the molecular diffusion. From last chapter, we already know the magnetic powered rotating objects are FMRCs rather than FMRs due to the clustering effect. However, we still use single rods instead of rod clusters to estimate the hydrodynamic effect to the molecular diffusion, because both of them can be treated as the micro rotators and induce the same flow patterns. The clustering effect will be discussed in last section of this chapter. If the rotating FMR is treated as a micro rotator driven by a torque $\vec{M}$ and equilibrium in a low Reynolds number flow, the induced convection are modeled as the Stokes' creeping flow surrounding with a concentrated torque $\vec{M}$, whose velocity is a function of radius $\vec{r}$

$$\vec{u} = \frac{\vec{\sigma} \times \vec{r}}{|\vec{r}|^3}. \quad (5.3)$$

Here, $\vec{\sigma}$ is the strength of the rotlet⁸

$$\vec{\sigma} = \frac{\vec{M}}{8\pi\eta}. \quad (5.4)$$

Thus, the velocity field induced by a rotating FMR can be expressed as

$$\vec{u} = \frac{\vec{M} \times \vec{r}}{8\pi\eta|\vec{r}|^3}. \quad (5.5)$$

According to Eq. (5.5), the induced velocity $\vec{u}$ decays with r^{-2} . For simplification, we assume the linear velocity at the circular surface encapsulating the rotating FMR is u_0 , as shown in Fig. 5.1(a). Then, the velocity at an arbitrary position (x, y) of the convection can be expressed as $u_x = -yu_0/r^3$ and $u_y = xu_0/r^3$. The conventional effect can be added to the molecular diffusion by integrating the local convection (u_x, u_y) with each step of the random

$$\text{walk, } \begin{cases} x_n = x_{n-1} + h \cos \theta_n + u_x(x_{n-1}, y_{n-1}) \\ y_n = y_{n-1} + h \sin \theta_n + u_y(x_{n-1}, y_{n-1}) \end{cases}, n = 1, 2, 3... \quad (5.6)$$

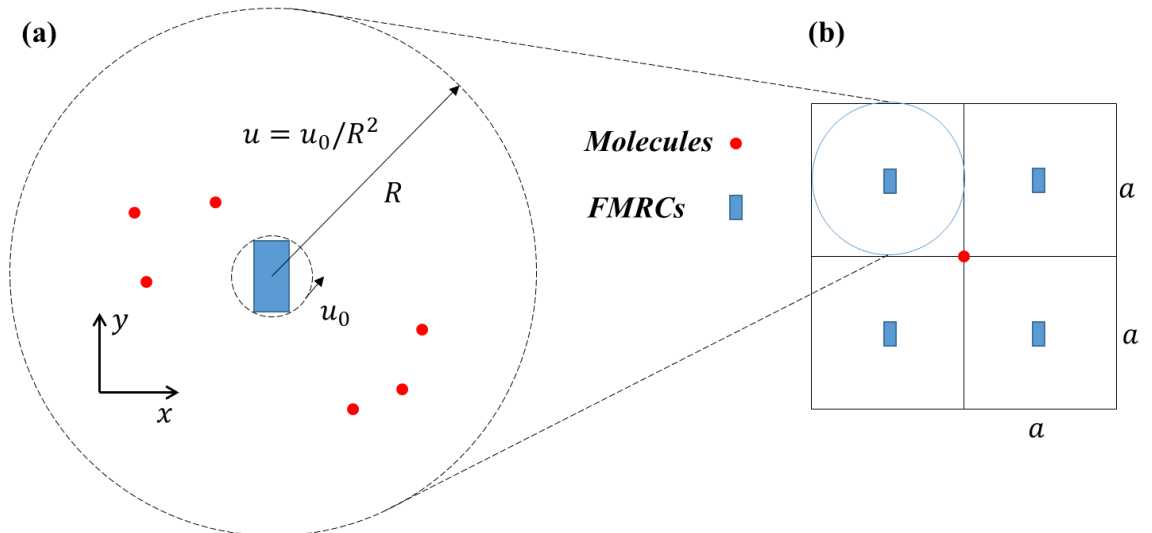


Figure 5.1 Molecular diffusion under convectional flow of the rotating FMRs (a) The flow field induced by a single FMR; (b) A molecule starts from the center of four FMRs.

To estimate collective effect of the rotating FMRs to the molecular diffusion, we further assume the FMRs are uniformly distributed in the water to form square lattices with an average space distance a . Figure 5.1(b) illustrates a square lattice consisting of four FMRs. a equals to the length of the grid occupied by a FMR, which is determined by the rod concentration C_R . Considering a molecule with an initial position at the center of the four FMRs as shown in Fig. 5.1(b), its trajectory can be simulated by Eq. (5.6). For simplification, we only consider the convections induced by these four FMRs and the local flow velocity is calculated from their superposition. In the simulation, the values of u_0 and a are normalized by step size h , where $h = 1$. Figure 5.2(a) depicts the trajectories (blue solid line) of 100 molecules experiencing $N = 1000$ step random walk in the convection induced by the FMRs with spacing distance $a = 100$. Most of the molecular trajectories are confined by the convections of the FMRs. From Eq. (5.1), the effective diffusivity of the molecules is estimated and plotted as a function against the velocity u_0 , as shown Fig. 5.2(b). As u_0 increases up to 10, the effective diffusivity monotonously increases from 0.4 to 0.8. However, when the concentration of the rod C_R increases, the FMRs get closer, leading to stronger convections. Figure 5.2(c) plots 100 molecular trajectories only in $N = 250$ steps when $a = 25$. All the other parameters are the same. From the trajectories, the molecules are dominated by the convection and start to translate surrounding FMRs. Meanwhile, the effective diffusivity D versus u_0 is plotted in Fig. 5.2(d), which increases up to 7-fold of the one without convections. From the comparison of Figs 5.2(b) and (d), one can see the rod concentration C_R is critical to the enhancement of the mass transport of the molecules.

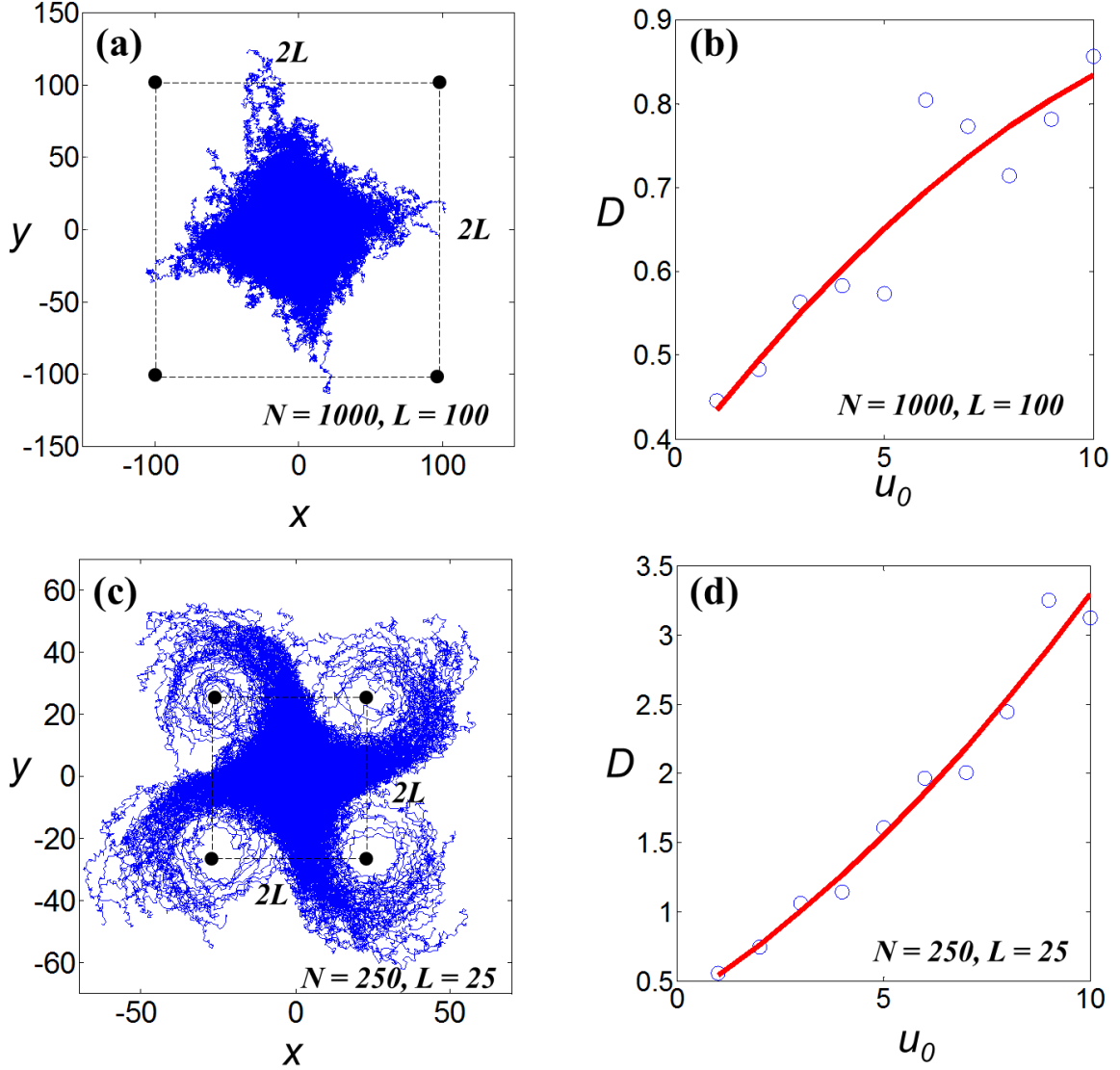


Figure 5.2 Simulated test of convection enhanced diffusivity by rotating rods. (a) Trajectories of 100 molecules in 1000 steps when $L = 100$ and (b) the effective diffusivity D versus v_0 ; (c) Trajectories of 100 molecules in 250 steps when $L = 25$ and (d) the effective diffusivity D versus v_0 . The red line is the polynomial fitting curve.

Since the rotating FMRs can enhance molecular diffusion, now we need study how this enhancement eventually translates to the acceleration of thrombolysis mediated by t-PA solution. Figure 5.3(a) illustrates the rotational rods at the vicinity of a clot, whose effective volume is a cylinder of a height d_R and a diameter d_R . Here, we assume the rod are uniformly distributed in three dimensions.

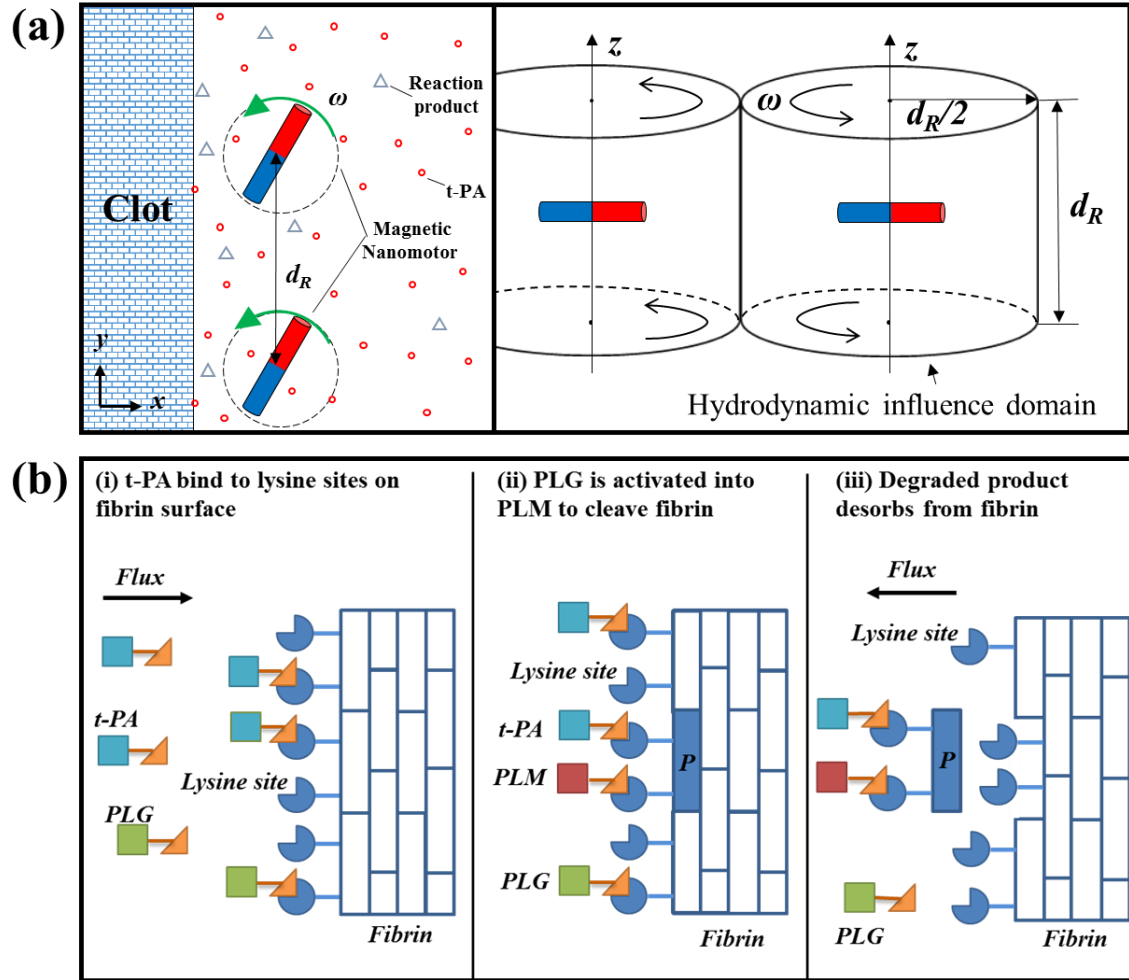
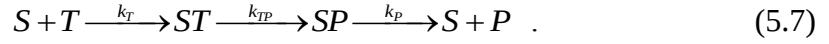


Figure 5.3 Schematic illustration of t-PA mediated thrombolysis enhanced by the FMRs at the liquid/clot interface. (a) Hydrodynamic induced mobility: When a FMR in solution is driven by a rotational magnetic field, it will induce a creeping Stokes' flow. The flow has a cylindrical hydrodynamic influence. The overall effect on the transport of t-PA and lysis molecules can be estimated as hydrodynamic agitation and provides an additional mobility besides thermal diffusion. (b) Simplified schemes of t-PA mediated thrombolytic reaction on clot surface: (i) t-PA and plasminogen molecules (PLG) diffuse to clot surface and bind to lysine sites. (ii) PLG molecules on the fibrin surface are activated into plasmin (PLM) by the neighboring t-PA molecules. PLM molecules start to cleave the local fibrin fiber into soluble products (P). (iii) Lysis molecules P leave fibrin surface and expose new lysine sites.

The detailed t-PA clot lysis process is shown in Fig. 5.3(b). The clot removed process is a classic mass transport governing reaction process, and it could be simplified into 3 sub-process: (1) t-PA molecules (T) diffuse to the fibrin surface and bind onto fibrin

lysine sites (S) to form t-PA-lysine complex (ST); (2) t-PA-lysine complex (ST) activates plasminogen into plasmin which cleaves fibrin into soluble product (P); (3) Product (P) desorbs from the fibrin surface and exposes new lysine sites, as proposed in Fig. 5.3(b) and expressed in Eq. (5.7)



where k_T is the adsorption rate of t-PA molecules on the fibrin surface and k_P is the desorption rate of product P removing from the fibrin surface. The process $ST \rightarrow SP$ involves multiple steps of bio-chemical reactions, and the intrinsic reaction rate is characterized by k_{TP} . The thrombolysis rate is determined by how fast sub-processes (1) – (3) happen sequentially and is dominated by the slowest sub-process. For different concentration of t-PA, the overall thrombolysis could either belong to a diffusion limited reaction or a reaction limited process. The rate of diffusion limited reaction would depend closely on the t-PA bulk concentration, while a reaction limited process will be independent on the t-PA concentration, as well known in all chemical reaction systems.

As shown in Eq. (5.7), assuming the coverage of ST on the surface is Θ_1 while the coverage of SP is Θ_2 , and the coverage for the vacant lysine sites should be $1 - \Theta_1 - \Theta_2$. Then the rate equations for Θ_1 and Θ_2 can be expressed as

$$\begin{cases} \frac{d\Theta_1}{dt} = k_T (1 - \Theta_1 - \Theta_2) - k_{TP} \Theta_1 \\ \frac{d\Theta_2}{dt} = k_{TP} \Theta_1 - k_P \Theta_2 \end{cases} . \quad (5.8)$$

The removal rate of product P with N_P available sites is

$$\frac{dN_P}{dt} = k_P \Theta_2 . \quad (5.9)$$

Under equilibrium, Eq. (5.8) gives

$$\begin{cases} \Theta_1 = \frac{k_T k_P}{k_T k_{TP} + k_{TP} k_P + k_P k_T} \\ \Theta_2 = \frac{k_T k_{TP}}{k_T k_{TP} + k_{TP} k_P + k_P k_T} \end{cases} \quad (5.10)$$

Combining Eqs. (5.9) and (5.10), we have

$$\frac{dN_P}{dt} = \frac{k_T k_P k_{TP}}{k_T k_{TP} + k_{TP} k_P + k_P k_T} \quad (5.11)$$

Equation (5.11) shows that the thrombolysis speed is determined by the reaction coefficients of all three steps in the thrombolytic model of Eq. (5.7). According to the experimental observation, however, if we consider a diffusion limited process, *i.e.*, $k_{TP} \gg k_T$ and $k_P \gg k_T$, Eq. (5.11) reduces to

$$\frac{dN_P}{dt} = k_T \quad (5.12)$$

If every productive molecule P frees a volume V_P from solid clot by dissolving process, then the observed clot dissolving speed in our experiments can be expressed as

$$v_{R+T} = \frac{V_P}{A_c (1-\Phi)} k_T, \quad (5.13)$$

where A_c is the cross-section area of the PDMS channel, Φ is the porosity of clot which can be assumed to be a constant. According to the von Smoluchowski's equation, the classic result of conjugation rate k_T between t-PA molecules and lysine sites is given as¹⁰⁸

$$k_T = 4\pi (D_{tpa} + D_{lysine}) (R_{tpa} + R_{lysine}) C_{tpa}, \quad (5.14)$$

where D_{tpa} and D_{lysine} represent the molecular diffusivities of t-PA and lysine site. R_{tpa} and R_{lysine} are the radii of t-PA molecules and lysine sites. C_{tpa} is the bulk t-PA concentration. Since the vacant lysine sites on clot surface are not moving, Eq. (5.14) becomes

$$k_T = 4\pi D_{tpa} (R_{tpa} + R_{site}) C_{tpa} . \quad (5.15)$$

From Eq. (5.15), the reaction rate k_T is proportional to the diffusivity D_{tpa} and the concentration C_{tpa} of t-PA molecules. Since C_{tpa} is limited in practice for the side effect of t-PA, D_{tpa} is our approach to accelerate the thrombolytic rate, as shown by the numerical simulation. Apparently, D_{tpa} contains two parts: thermally induced diffusion D_{tpa}^T and convectional flow enhanced diffusion by rotating rods D_{tpa}^C ¹⁰⁹⁻¹¹⁰

$$D_{tpa} = D_{tpa}^T + D_{tpa}^C . \quad (5.16)$$

D_{tpa}^T can be estimated from Einstein's theory Eq. (1.16), while the expression of D_{tpa}^C depends on the Peclet number, according to convection theory, When the Peclet number Pe is small ($Pe < 3$),¹⁰⁹ the flow scaling law is valid for rigid-boundary conditions and the convectional flow enhanced diffusivity D_{tpa}^C in Eq. (5.16) can be estimated as¹¹⁰⁻¹¹¹

$$D_{tpa}^C = aPe^2 D_{tpa}^T , \quad (5.17)$$

where a is a constant regarding to the flow field and Pe is the Peclet number defined as

$$Pe = \frac{\bar{u} d_R}{D_{tpa}^T} , \quad (5.18)$$

where $\bar{u}$ is the average velocity of the flow field and $d_R = C_{NR}^{-1/3}$ is the size of each cellular flow induced by a rotating FMR (Fig. 5.3(a)). For the convenience of derivation, C_{NR} is the number concentration of rods. If more than one FMR is put in the liquid with a uniform distribution and applied by an equal driven torque M , the flow velocity by multi-rotating rods can be averagely estimated as

$$\bar{u} = \frac{\sum_{i=1}^n \int_{\Omega_i} |\vec{u}| d\Omega}{V_L} = \frac{|\vec{M}| C_{NR}^{2/3}}{4\eta} \ln(1 + \sqrt{2}), \quad (5.19)$$

where $\bar{u}$ is the velocity induced by a single rod of Eq. (5.5), $\Omega_i = \pi d_R^3 / 4$ is the hydrodynamic volume of a single rod, V_L is the total volume of the liquid. At the low Reynolds, the singular point torque $|\vec{M}|$ by a rotating FMR equals to the hydrodynamic drag torque on it (Eq. (1.8))

$$\vec{M} = \frac{-2\pi\epsilon_\perp l^3 f}{3}, \quad (5.20)$$

Combining Eq. (5.15) with (5.20), the reaction rate of thrombolysis k_T can be theoretically increased by the convection flow of rotating FMRs. Among all the parameters related to the induced conventions, the rotating frequency f and the rod concentration C_R can increase the conventions. However, the clustering effect cannot be neglected according to our previous study in Chapter 4. At higher frequency, the FMRC becomes smaller, whose hydrodynamic effect is difficult to predict. On the other hand, the rod concentration C_R is positively correlated with $\bar{u}$, which has been proved numerically. Combining Eqs. (5.13) – (5.19), the theoretical prediction of thrombolysis observed in our experiments is expected to the following relation with respect to FMR concentration C_R

$$v_{R+T} = v_T + \alpha C_R^{2/3}, \quad (5.21)$$

$$\text{where } v_T = \kappa C_{tpa} D_{tpa}^T, \text{ where } \kappa = \frac{4\pi(R_{tpa} + R_{site})V_P}{A_C(1-\Phi)}, \text{ and } \alpha = \kappa C_{tpa} \frac{0.0486a|\vec{M}|^2 \chi^{2/3}}{\eta^2 D_{tpa}^T}.$$

When $C_R = 0$, Eq. 5-42 degrades to

$$v_T = \kappa C_{tpa} D_{tpa}^T. \quad (5.22)$$

Here, the thrombolysis speed v_T (without rods) is proportional to C_{tPA} .

5.2 Experimental Methods

As illustrated in Fig. 5.4(a), the proposed strategy is to mix t-PA solution with FMRs' suspension, and to rotate the FMRs remotely by a rotating magnetic field. We expect that the rotating nanorods can enhance the t-PA thrombolysis speed through enhanced mass transport. The proof-of-concept experiments were carried out in PDMS

channels, as shown in Fig. 5.4(a). The PDMS was mixed with the solidify agent and poured in an aluminum mold after degassing in vacuum. Cured in an oven at 72°C for 2 hours, the PDMS plate was peeled off from the mold. Then it was covalently bonded with another blanket flat PDMS plate to form the experimental plate with 8 comb-like $2 \times 1 \text{ mm}^2$ rectangular channels, as shown in Fig. 5.4(b). Two rows

of 1-mm diameter holes were punched at 10 mm and 20 mm from the open ends. The first row of holes was used to inject the reaction solution and the second row was used for the mineral oil to seal the reaction solution within the channels and prevent evaporation. To fabricate length-controlled clot in the PDMS channels, all the reagents and the channels were cooled in an ice box at 0°C for 15 min. Then, $80 \mu\text{l} \times 1 \mu\text{M}$ human thrombin (Thrombin from human plasma, Sigma-Aldrich) was

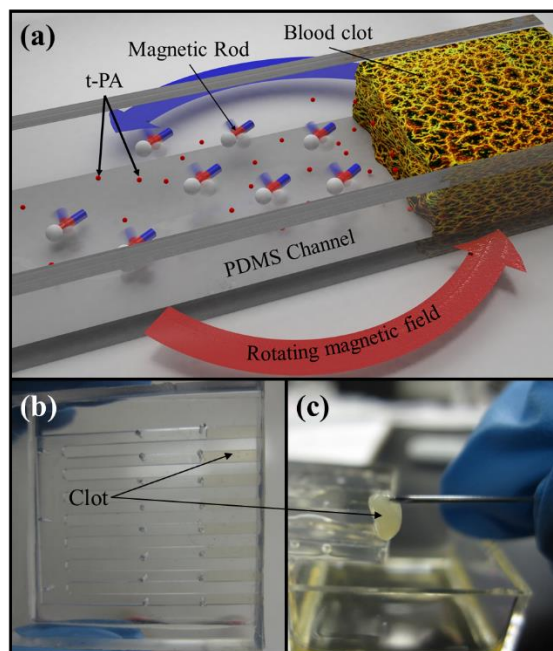


Figure 5.4 Illustration of *in-vitro* experiments in PDMS channels (a) Schematic graphic of FMRs working at the vicinity of a clot. (b) Channels plugged with clot, shown as light-yellow segments. (c) A clot pricked from a PDMS channel after fully reaction.

added to 1 ml HPPP (Human Platelet Poor Plasma, Innovative Research), mixed by vortex. Since the enzyme catalytic reaction was slowed down at the low temperature, the mixture remained as a flow-able “clot” in about 1 min. Within this time, a 20 μ l well-mixed thrombin and HPPP was injected from the end of each channel one by one to form a 10 mm long clot. Once the mixture was injected in the channels, it could not flow out due to the capillary force. Then the plate was immediately suspended in a pool of 4 mL HPPP at 37 °C for 20 minutes. This allowed the residual agents in channels to continue reacting with HPPP sufficiently and reinforce the clot structures. After this process, the open ends of the device were sealed by epoxy and ready for the injection of reaction solution. As shown in Fig. 5.4(b) and (c), uniform and equal-length clots were fabricated. Fig. 5-12(b) also shows the tangled clot after it was removed from a channel after fully reacted.

Once the clot was created in the channel, the reaction solution was injected to the left of the clot sections and sealed by mineral oil from the left end to prevent solution evaporation during the experiments (Fig. 5.5(a)). The composition of the reaction solution is FMRs suspension, t-PA solution and pure water. Here, we use nickel rods as FMRs, whose fabrication and preparation were introduced in Section 5.3. The t-PA solution was mixed with deionized water (Alteplase, Genentech) and adjusted to different concentration. A dye (Rhodamine B, Sigma-Aldrich) was added to all the reaction solution and tuned to a final concentration of 0.5 mM, in order to improve the data visualization. The experimental setup in Fig. 4.3(a) consists of a magnetic field generator, a PDMS plate with test samples inside, a light pad, and a data acquisition system. A rotational magnetic field of $B = 8$ mT, $f = 20$ Hz is generated by the coils. The PDMS plate was suspended at the center of the solenoids by a glass slide with printed scales (green-dash lines), and was

placed above a light pad (LightPad A920, Artograph) which provides a uniform and stable white light illumination. Images were obtained via a digital camera (Infinity 1, Lumenera) with a zoomable lens (Zoom 7000, Navitar).

5.3 Results and Discussions

Figure 5.5(a) shows the top view of the PDMS channels under experiments. To test the effect of rotating FMRs, four different solutions were injected to the PDMS channels: dye solutions, denoted as “*D*”; t-PA mixed with dye solution, denoted as “*T*”; FMRs-dye mixture solution, denoted as “*R*”; and dye, t-PA, and FMRs mixture solution, denoted as “*R+T*”, as shown in Fig. 5.5(a). Figure 5.5(a) also shows the representative snapshots of the moving t-PA/clot interfaces at different time. All interface fronts in the “*R*” and “*D*” channels remain almost fixed while the interfaces at all the “*T*” and “*R+T*” channels advance to the right. It is observed that the interfaces of the “*R+T*” channels move faster than those of the “*T*” channels. Figure 5.5 (b) plots the one-dimensional grayscale distribution of dye along four representative channels at four different times. The lysis speed in each channel was assumed to be proportional to the boundary moving speed. For both the “*D*” and “*R*” channels, the gray scale profiles show diffusion like behavior. The boundaries move slightly, but the profiles become more broadened. Using the dye concentration calibration curve with respect to the gray scale, and taking the first derivation of the profile, one can obtain how the dye moving into the clot. From the width versus time plot in “*D*” channel, we can extract the diffusion coefficient of dye to be $27.7 \pm 0.6 \mu\text{m}^2/\text{s}$. For the “*R*” channel, the obtained diffusion coefficient to be $42.4 \pm 0.6 \mu\text{m}^2/\text{s}$, which is

slightly larger than that in “D” channel. This is an indication of rotating FMRs enhanced molecular diffusion.

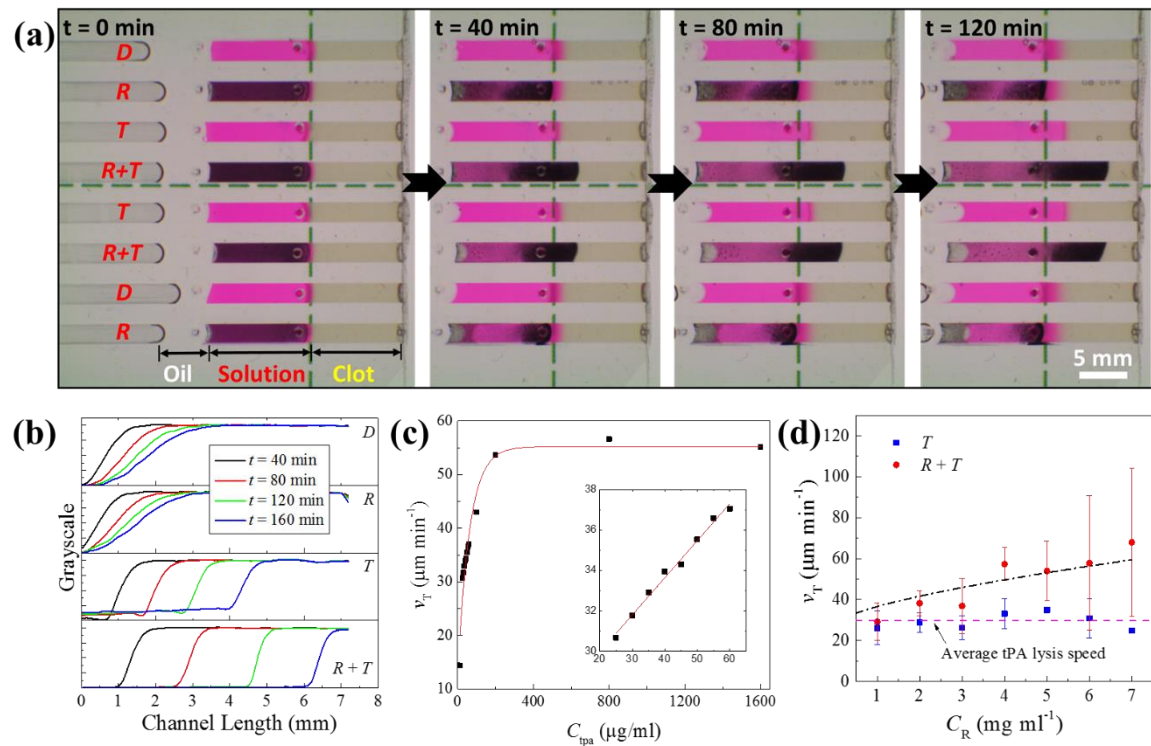


Figure 5.5 Results of *in-vitro* experiments: (a) A representative PDMS channel images. (b) The plot of gray scale at different thrombolysis time $t = 40, 80, 120$, and 160 min (from left to right), in the “D”, “R”, “T”, “R+T” channels (from top to bottom). (c) The clot boundary moving speed v_T versus the t-PA concentration C_{tpa} in “T” channel. (d) Clot boundary moving speed v_T and v_{R+T} versus FMR concentration C_R . The blue solid square “■” represents v_T and the red solid circle “●” represents v_{R+T} . The pink dash line is a guide to eyes, and black dash-point curve is a fitting curve based on the proposed theoretical model.

This is further confirmed by the *in vitro* thrombolysis carried in the “T” channels by the pure t-PA solution, whose concentration varies from 12.5 $\mu\text{g/ml}$ to 1600 $\mu\text{g/ml}$. It is observed that the dye/clot interface of all channels advance to the right, *i.e.*, to the clot section. The experiment results are summarized in Fig. 5.5(c). At low C_{tpa} (≤ 60 $\mu\text{g/ml}$)

the clot lysis speed v_T increases almost linearly with C_{tpa} . And when $C_{tpa} \geq 200 \mu\text{g/ml}$, v_T reaches a maximum value of $55 \mu\text{m/min}$. Thus at $C_{tpa} \leq 60 \mu\text{g/ml}$ (clinically administrative t-PA concentration), of the thrombolysis process is a diffusion limited process. Therefore, in order to enhance the thrombolysis but keep the t-PA concentration low, it is important to improve the mass transport process during thrombolysis, and we believe that such a mass transport enhancement can be achieved by rotating FMRs.

To test the effect of FMRs, the C_{tpa} in “ T ” and “ $R+T$ ” channels is designed to be the same, $50 \mu\text{g/ml}$. In both “ R ” and “ $R+T$ ” channels the FMRs concentration C_R has been changed systematically from 1 to 7 mg/ml. For both “ T ” and “ $R+T$ ” channels, the gray scale profile maintains its overall shape, but advances to the right quickly. Clearly, the “ $R+T$ ” profile advances faster than the “ T ” profile. In fact, for $C_R = 7 \text{ mg/ml}$, the average thrombolysis speed v_T for “ T ” channel is $24.8 \pm 0.5 \mu\text{m/min}$, and the average enhanced thrombolysis speed v_{R+T} in “ $R+T$ ” channel is $68 \pm 36 \mu\text{m/min}$, as shown in Fig. 5.5(b). This speed is close to the maximum lysis speed at very high t-PA concentration ($C_{tpa} \geq 100 \mu\text{g/ml}$). By varying the FMRs concentration C_R and keep all the other conditions constant, one observes that the thrombolysis speed v_{R+T} increases monotonically as a function of rods concentration C_R . Figure 5.5(d) plots v_T and v_{R+T} versus C_R . One can see that at different C_R , v_T fluctuates within $29 \pm 6 \mu\text{m/min}$ while v_{R+T} increases monotonically with C_R .

According to Eq. (5.20) For a rod of length $l = 1 \mu\text{m}$ and diameter $d = 0.5 \mu\text{m}$ rotating at frequency $f = 20 \text{ Hz}$, the induced torque $\vec{M} = 3.97 \times 10^{-18} \text{ N} \cdot \text{m}$. With all known

conditions, for example, when $C_R = 7 \text{ mg/mL}$, the highest concentration used in our experiments, the average hydrodynamic velocity induced by rotating rods $\bar{u}$ is about $11 \text{ } \mu\text{m/s}$; while $C_R = 1 \text{ mg/mL}$, $\bar{u} = 3 \text{ } \mu\text{m/s}$. Since the diameter of t-PA soluble molecule is about 10 nm ,¹¹² the thermal diffusivity of t-PA molecules without rods is $D_{tpa}^T = 4.5 \times 10^{-11} \text{ m}^2 / \text{s}$, estimated by Eq. (1.16). According to results of Eq. (5.18), the Peclet number Pe varies from 1.6 to 3.1 when C_R changes from 1 to 7 mg/ml in our experiments. Therefore, Eqs. (5.17) and (5.21) are valid to model our experimental results. According to Eq. (5.22), the thrombolysis speed v_T without rods is proportional to C_{tpa} . This has been verified in the region of low concentration of t-PA, as shown in Fig. 5.5(c). $C_{tpa} = 50 \text{ } \mu\text{g/ml}$ for the rod enhanced thrombolysis is in the linear region of our experiments. Thus, the coefficient κD_{tpa}^T in Eq. (5.22) can be extracted from the slope of the curve in the linear region as shown in the insert plot, and we obtain $\kappa D_{tpa}^T = 3.03 \times 10^{-6} \text{ m}^4/\text{kg}\cdot\text{s}$, and $\kappa = 6.69 \times 10^4 \text{ m}^2/\text{kg}$. As shown in Fig. 5.5(d), the experimental data of v_{R+T} (red circle) is well fit by Eq. (5.21) (black dash line). We obtain $\alpha = (9 \pm 2) \times 10^{-4} \text{ ml/mg}^{2/3} \cdot \text{min}$ that is on the same order of magnitude estimated by Eq. (5.21). The match between the theoretical prediction and experimental data further validates the mechanism of enhanced mass transport for thrombolysis.

However, we also notice that the error bar of v_{R+T} increases by C_R in Fig. 5.5(d). This is mainly caused by the size variation of FMRCs, which was studied under different field conditions in the section 4.3. Here, we conducted an experiment to observe the FMRCs size at different concentrations under the same field condition. Figure 5.6 shows the average size of FMRCs versus FMR concentration for our experiments.

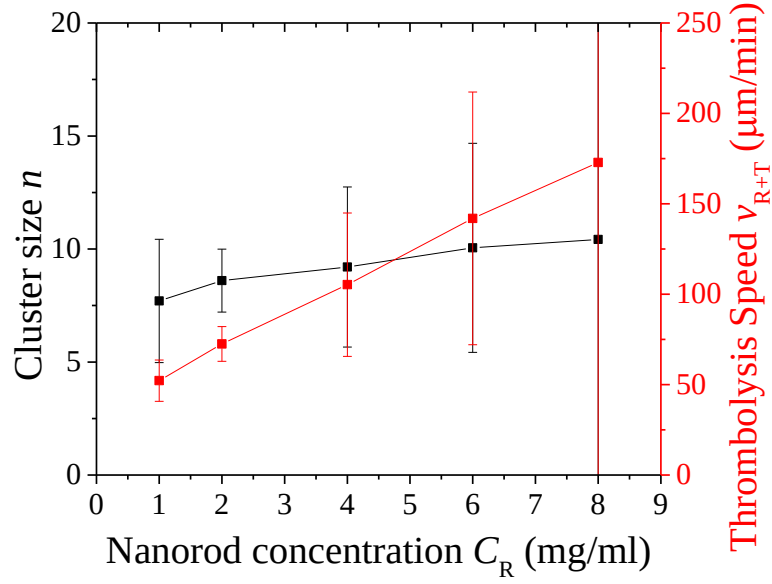


Figure 5.6 The FMRCs' size distribution (black) and the theoretical prediction of the upper-bound thrombolysis with uncertainties (red) versus different FMR concentration C_R

From Fig. 5.6, the average cluster size $n = C_{NR} / C_{cluster}$, defined as the average number of FMR in a FMRC, increases by the rods concentration. Note that the error bar of cluster size n is up to ± 17.28 , and theoretical thrombolysis speed v_{R+T} is up to ± 327.51 $\mu\text{m}/\text{min}$ at $C_R = 8$ mg/ml. If each FMRC is treated as an individual rotor, Eq. (5.21) can be modified as

$$v_{R+T} - v_T = \Delta v = \alpha_{FMRC} C_{FMRC}^{2/3} = \kappa C_{tpa} \frac{0.0486a |\vec{M}|_{FMRC}^2 C_{FMRC}^{2/3}}{\eta^2 D_{tpa}^T}, \quad (5.23)$$

where $|\vec{M}|_{FMRC}$ and C_{FMRC} are the torque induced by a single FMRC and the concentration of the torques, both depend on the FMRC size. However, it is difficult to estimate the magnitude of $|\vec{M}|_{FMRC}$ using the hydrodynamic drag torque because the arrangement of rods

in a cluster is unknown. Thus, we cannot simply use the relation $|\vec{M}|_{cluster} = \sum |\vec{M}|_{rod}$

However, we can still apply the 1D chain model for the estimation for the upper boundary

$$\left| \vec{M} \right|_{cluster} \leq n \left| \vec{M} \right|. \quad (5.24)$$

Plug Eq. (5.24) into Eq. (5.23), we have

$$\Delta v \leq \frac{0.0486 a \kappa C_{tpa} \left| \vec{M} \right|^2 C_{NR}^{2/3}}{\eta^2 D_{tpa}^T} n^{4/3} = \alpha' C_{NR}^{2/3}, \quad (5.25)$$

where $\alpha' = \alpha n^{4/3}$ is the new proportionality of enhanced thrombolysis Δv with respect to $C_{NR}^{2/3}$ due to the presence of cluster. Then we can estimate the error bar of v_{R+T} using the uncertainty of FMRC size

$$\delta v_{R+T} = \left| \frac{\partial \Delta v}{\partial n} \cdot \delta n \right| \leq \frac{4}{3n} \alpha' C_{NR}^{2/3} \delta n. \quad (5.26)$$

According to Eq. (5.26) and Fig. 5.6, the error bar of thrombolysis is predicted to increase by the FMR concentration C_R , which is consistent with experimental data in Fig. 5.5(d). Moreover, the item of $n^{4/3}$ in Eq. (5.25) suggests the elevation of thrombolysis due to the hydrodynamic effect of FMRCs rather than FMRs.

Our model also indicates that the rotation of FMRCs near the clot/solution interface should be more effective compared to locations far away from the interface. This means local concentration of the FMRs at the fibrin interface is important in achieving faster clot removal rate. We designed an experiment to demonstrate this effect. The *in-vitro* experiment at $C_R = 1$ mg/ml was repeated with all the other experimental conditions fixed, except adding an iron nail at the right end of the PDMS device, close to the clot segments. Due to the higher magnetic permeability of the nail, there is a local field maximum of magnetic field attracting FMRs toward the clot interface and makes them stay at the

clot/solution boundary during the experiment. Thus, the local concentration of rods at the clot/solution interface is greatly increased.

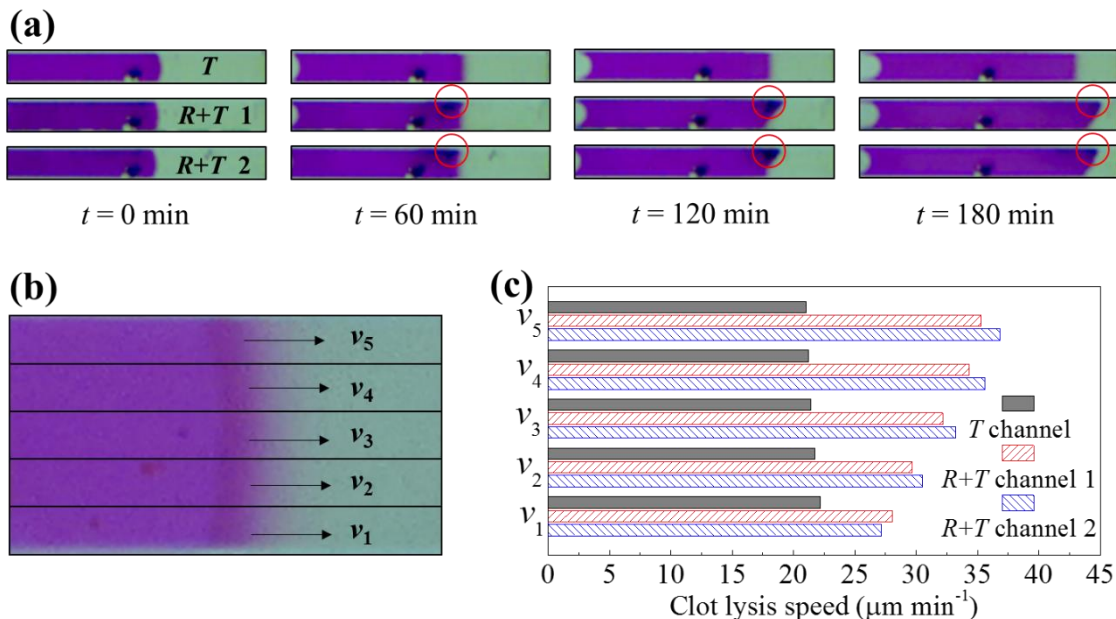


Figure 5.7 Locally enhanced thrombolysis through concentrating Nanorods: (a) Video clips of dye-solution/clot interface evolution in one “T” and two “R+T” channels with $C_R = 1$ mg/ml with a nail presented in the magnetic field. Red circles indicate locations of the concentrated magnetic nanorods. (b) Each channel is horizontally divided into 5 sub-channels of equal width, and the moving speed of liquid/clot interface in each sub-channel is labeled as v_1 , v_2 , v_3 , v_4 , and v_5 , from bottom to top. (c) The local clot lysis rate of three channels. Due to the conjugation of nanorod at the top right corner in two “R+T” channels, the lysis rate is increased from v_1 to v_5 . The enhanced thrombolysis factor β can be up to 1.75 which is comparable to v_{R+T} at $C_R = 5$ mg/ml shown in Fig. 5.5 (d).

As shown in Fig. 5.7(a), the rods are uniformly distributed in the “R+T” channels at $t = 0$ min. When the magnetic field is on, the FMRs are concentrated at the clot boundaries and form a taper-shape. To evaluate the location-dependent thrombolysis rate, each channel in Fig. 5.7(a) is horizontally divided into 5 sub-channels of equal width, as shown in Fig. 5.7(b) of the “T” channel. The moving speeds of liquid/clot interface at different sub-channels, from bottom to top, are estimated as v_1 , v_2 , v_3 , v_4 and v_5 . According to the results shown in Fig. 5.7(c), the thrombolysis rates v_T in sub-channels of “T” are very

uniform with an average value of $22.2 \pm 0.1 \mu\text{m}/\text{min}$. Remarkably, the thrombolysis rates v_{R+T} in sub-channels of “ $R+T$ ” increases from v_1 to v_5 due to the gradual accumulation of FMR toward the up-right corner at the boundary. The maximum thrombolysis rate v_{R+T} at different location in “ $R+T$ ” channels is up to $36.8 \pm 0.4 \mu\text{m}/\text{min}$. Thus, the enhanced thrombolysis factor $\beta = v_{R+T} / v_T$ can be up to 1.66. However, for $C_R = 1 \text{ mg/ml}$ with uniform FMR distribution shown in Fig. 5.7(d), $v_{R+T} = 29 \pm 9 \mu\text{m}/\text{min}$ while $v_T = 26 \pm 8 \mu\text{m}/\text{min}$, and $\beta = 1.1$. Thus, for the same C_R , the thrombolysis enhancement by rods concentrated at the clot/solution interface ($C_R = 1 \text{ mg/ml}$) is significantly larger. In fact, the β of local-concentrated rods with $C_R = 1 \text{ mg/ml}$ is comparable to that of $C_R = 5 \text{ mg/ml}$ with uniform FMR distribution, as shown in Fig. 5.5(d). The results demonstrate that by concentrating magnetic FMRs at the clot/liquid interface, even with a low C_R , the v_{R+T} can be significantly improved. This feature would reduce the potential side-effect caused by FMRs for clinical application.¹¹³

5.4 Conclusions

In this chapter, we developed a novel active nanomotor-based method to directly enhance t-PA mediated thrombolysis. Compared with nano-carrier based strategies that focus on the loading rate of specified drug molecules to specified nano-carriers, active motions of nanomotors accelerate the thrombolysis by elevating drug transport through a hydrodynamic convection, which was verified both theoretically and numerically. The *in-vitro* experiments demonstrated that when combined with magnetically activated

nanomotors, the thrombolysis speed of low concentration t-PA (50 $\mu\text{g/ml}$) could be enhanced up to two-fold, to the maximum lysis speed at high t-PA concentration.

CHAPTER 6

SUMMARIES AND FUTURE WORK

This dissertation presents a fundamental study of the dynamic behaviors and the structural transitions of FMRCs under different magnetic fields. We envision that the knowledge from this dissertation might enable new applications and technologies in stroke treatment, as shown in Figure 6.1. For example, the structure changes of FMRCs under magnetic fields might be used a way to encapsulate and release drugs on-demand; the rotations of FMRCs under magnetic fields might be applied to enhance mass transport of t-PA drug, which was demonstrated *in-vitro* in this dissertation; finally, the interesting stripy pattern developed under magnetic fields might have implications in cell patterning and potentially brain tissue reconstruction.

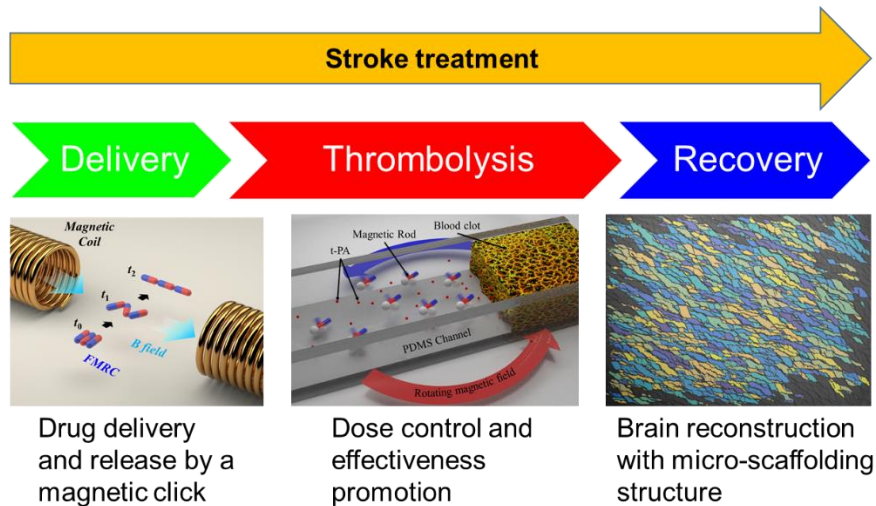


Figure 6.1 Potential applications of FMRCs for the stroke treatment.

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