Effects of magnetic nanoparticles on mixing in droplet-based microfluidics

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Abstract

High-throughput, rapid and homogeneous mixing of microdroplets in a small length scale such as that in a microchannel is of great importance for lab-on-a-chip applications. Various techniques for mixing enhancement in microfluidics have been extensively reported in the literature. One of these techniques is the mixing enhancement with magnetofluidics using ferrofluid, a liquid with dispersed magnetic nanoparticles. However, a systematic study exploring the mixing process of ferrofluid and its influencing parameters is lacking. The present study numerically examines the effect of key parameters including magnetic field,

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mean velocity and size of a microdroplet on the mixing process. A microfluidic double T-junction with droplets in merging regime is considered. One of the dispersed phases is a ferrofluid containing paramagnetic nanoparticles, while the other carried neutral species. Under an applied magnetic field, the ferrofluid experiences a magnetic force that in turn induces a secondary bulk flow called magnetoconvection. The combination of the induced magnetoconvection and shear-driven circulating flow within a moving droplet improves the mixing efficiency remarkably. Mixing enhancement is maximized for a specific ratio between the magnetic force to the shear force. The dominance of either force would deteriorate the mixing performance. On the other hand, using a magnetic force and a shear force with comparable order of magnitude leads to effective manipulation of vortices inside the droplet, and subsequently causes an optimized particles distribution over the entire droplet. Furthermore, the smaller the droplets are the better is mixing.

I. INTRODUCTION

Microfluidic technology holds a great potential for biomedical applications. This technology allows for implementing laboratory operations using a small volume of reagents in a short time.¹ Droplet-based microfluidics is an important branch of microfluidics, where discrete droplets are handled within an immiscible carrier fluid. Because of the encapsulation and protection of the droplets by the surrounding immiscible fluid, such systems can function as a sample test tube or a microreactor in small scale.² Droplet-based microfluidics has several advantages over continuous-flow microfluidics, including the elimination of cross-contamination of the analytes, ultra-high-throughput screening process, a significant reduction in consumption of reagents due to the small volume of the droplets, the capability of high throughput generation, manipulation, and processing of ultra-small microreactors.³ These advantages lead to the growing use of droplet-based

microfluidics in applications such as studying cell mechanical behavior and tissue aspiration,⁴ drug screening and discovery,⁵ chemical and biochemical synthesis,⁶ DNA and genomic studies,⁷ cell culture,⁸ and diagnostics.⁹

However, high-throughput combinatorial assays in droplet-based microfluidics require the implementation of multiple steps such as compartmentalization, manipulation and measurement.¹⁰ Most useful operations are droplet generation,¹¹ transport,¹² sorting,¹³ separation,¹⁴ merging,¹⁵ trapping¹⁶ and mixing the droplet contents.^{4, 17} Diverse mechanisms have been employed for droplet handling such as electrowetting,¹⁸ dielectrowetting,¹⁵ magnetofluidic,¹⁹ photoactuation,²⁰ hydrodynamic,¹⁰ surface acoustic waves,² chemical gradient,²¹ surface morphological gradients²² and temperature gradient.²³

Mixing is one of the basic microfluidic operations that plays a crucial role in the above applications. Nevertheless, obtaining uniform mixing in microfluidic devices in a short time has been challenging because of the low Reynolds number of the resulting laminar flow in microchannels.²⁴ Due to the more rapid mixing process of microdroplet in a multi-phase system compared to that in a single-phase system and their advantage in elimination the dispersion effect, microdroplets are frequently used to enhance mixing in microfluidics.²⁵ Traditionally, mixing inside droplets is enhanced using chaotic advection. In a straight channel, developing a chaotic flow in droplets is challenging due to the symmetric internal flow recirculation.

Therefore, various experimental and numerical studies have been conducted to improve the mixing performance of droplet-based microfluidics, using either passive or active techniques.^{17, 26, 27} In passive mixers, chaotic advection inside the droplet is introduced by passing the droplet through serpentine, sinusoidal and meandering microchannels. A droplet traveling in a curved microchannel establishes asymmetric recirculation, which allows for convective mass transfer

enhancement in both axial and radial directions.²⁸ While passive micromixers include the intricate structure of microchannel or long mixing length to achieve the desired mixing output, active mixers utilize external energy to induce flow disturbance to enhance mixing.²⁹ Exploiting magnetic force is a convenient technique because of advantages such as convenient bio-functionalizing of magnetic particles, remote control and straightforward design.^{24, 26} Combining magnetism and fluid flow in the microscale for actuation and sensing applications led to the field of micro magnetofluidics.³⁰

Several studies devoted to mixing within microdroplets using magnetic particles. Part of these studies investigated droplets merging and mixing using magnetic nano/microparticles on digital micro magnetofluidic platforms.³¹ Even though digital platforms provide the possibility of precise control and manipulation of a single droplet, their low throughput may prevent them from applications such as drug screening, where a large number of droplets are manipulated simultaneously. Magnetic stirring inside a droplet is an alternative strategy for mixing enhancement. Magnetic polymer beads,³² polymer structures containing magnetic nanoparticles,²⁶ and magnetic bars have been used for stirring inside droplets. In this technique, the dipole-dipole interaction between magnetic particles in the presence of a magnetic field causes the formation of a particle chain forming the stirrer. These structures are actuated by an external rotational magnetic field leading to mixing inside a droplet. Sedimentation of large magnetic stirrers and the need for a very strong magnetic field for smaller stirrers are the main problems of this approach.²⁶ Despite the above experimental works, there is a lack of detailed study that numerically investigates magnetofluidic mixing process of ferrofluid and its efficiency.

Herein, we numerically evaluate the influence of the magnetic field and inhomogeneous magnetic fluid on the mixing process within a microdroplet. The concentration gradient of magnetic particles

inside the droplet lead to magnetic moment gradient and consequently a magnetic bulk force, even in a uniform magnetic field. The induced magnetic force contributes to a secondary flow inside the droplet when it is passing through a straight channel. This secondary flow makes the internal circulations asymmetric, leading to chaotic advection and significant mixing enhancement. We first compare droplet mixing with and without a magnetic field, where we consider ferrofluid as one of the dispersed phases. We will show that the magnetic field can be very beneficial for significantly enhancing the mixing process inside the droplet.

II. MATHEMATICAL MODELING AND IMPLEMENTATION

A. Governing equations and boundary conditions

Incompressible Navier-Stokes equation is employed to describe the flow dynamics:³³

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla) \mathbf{u} = -\nabla p + \eta \nabla^2 \mathbf{u} + \mathbf{F}_s + \mathbf{F}_m \quad (1)$$

In this equation, ρ represents the density of the fluid, p the pressure, η the dynamic viscosity and $\mathbf{F}_s$ the force caused by surface tension and $\mathbf{F}_m$ the magnetic volume force. Surface tension body force $\mathbf{F}_s$ is calculated as:³⁴

$$\mathbf{F}_s = \nabla \cdot \left(\sigma \left(\mathbf{I} - (\mathbf{n} \mathbf{n}^T) \right) \delta \right) \quad (2)$$

where $\mathbf{n}$ is a unit vector that is normal to the interface, σ is the interfacial tension between the two phases and δ is delta function with zero value in all domain except fluids interface. This function is expressed as follow:

$$\delta = 6 |\nabla \phi| |\phi(1-\phi)| \quad (3)$$

Where φ represents the level-set function that is used to model the interaction of immiscible fluids and govern their interface movement. In the level-set method, the level-set function φ determines the distinct phases and portrays a smooth transition across the interface from one to zero by a Heaviside function,³⁴ the conservative level set equation is defined as follow:

$$\frac{\partial \varphi}{\partial t} + \mathbf{u} \cdot \nabla \varphi = \gamma \nabla \cdot \left(\varepsilon \nabla \varphi - \varphi(1 - \varphi) \frac{\nabla \varphi}{|\nabla \varphi|} \right) \quad (4)$$

where γ represent the reinitialization parameter and the ε denotes interface thickness where level set function vary from 0 to 1 (for core $\varphi = 1$ and for carrier $\varphi = 0$). Reinitialization is a necessary step to maintain the signed distance property and control the numerical stabilization.

The following convective/diffusive equation describes the non-dimensional mass transport throughout the fluidic domain; this equation is used to model the distribution of magnetic particles in the computational domain:³⁵

$$\frac{\partial c}{\partial t} + \mathbf{u}_p \cdot \nabla c = \nabla \cdot (D \nabla c) \quad (5)$$

where c represents dimensionless concentration, D denotes diffusivity coefficient and $\mathbf{u}_p$ denotes the velocity of the particles. The diffusive behavior of the magnetic particles is affected by magnetic force. This effect is shown by an additional velocity component that is given by Stokes drag law:

$$\mathbf{u}_p = \mathbf{u} + \mathbf{u}_{mag} = \mathbf{u} + \mathbf{F}_{mag} / 6\pi\eta r_p \quad (6)$$

129 where r_p shows magnetic particle radius and $\mathbf{F}_{mag}$ is the magnetic force on each particle which is
 130 given by:

$$131 \quad \mathbf{F}_{mag} = \frac{1}{2} V_p \mu_0 \nabla \chi \mathbf{H}^2 \quad (7)$$

132 where V_p is the volume of any single magnetic particle, μ_0 is the permeability of the vacuum space,
 133 χ is the local susceptibility of the ferrofluid and $\mathbf{H}$ is the magnetic field strength.

134 Considering the distinct solubility of species (i) in each phase, there is a concentration jump across
 135 the fluid interface. The interfacial discontinuity of concentration can be expressed as follow:³⁶

$$136 \quad c_c = K c_d \quad (8)$$

137 where K is the distribution coefficient. The indices c and d correspond to the continuous and
 138 dispersed phase, respectively. In addition, flux continuity condition is established at the interface:

$$139 \quad D_d \frac{\partial c_d}{\partial \mathbf{n}} = D_c \frac{\partial c_c}{\partial \mathbf{n}} \quad (9)$$

140 Because of the moving interface, it is difficult to apply the boundary condition to this area. Keniga
 141 et al.³⁴ suggested a new method to address this problem. This method incorporates interfacial
 142 boundary conditions to the mass transport equation so that these conditions are satisfied only in
 143 the proximity of the immiscible fluids interface. Considering the above boundary conditions, new
 144 source terms are added to the mass transport equation. Accordingly, the following equations are
 145 obtained and solved for all the fluidic domains:

$$\frac{\partial c_d}{\partial t} + \mathbf{u}_p \cdot \nabla c_d = \nabla \cdot (D \nabla c_d) + \alpha_1 \left(D_c \frac{\partial c_c}{\partial \mathbf{n}} - D_d \frac{\partial c_d}{\partial \mathbf{n}} \right) \quad (10)$$

$$\frac{\partial c_c}{\partial t} + \mathbf{u}_p \cdot \nabla c_c = \nabla \cdot (D \nabla c_c) + \alpha_2 \left(c_c - \frac{c_d}{K} \right) \quad (11)$$

To fulfill the boundary condition at the interface, the values of α_1 and α_2 should be considered as large enough at the interface and zero in other places. For this purpose, we have implemented a multiple of Dirac distribution³⁷ of the level set φ variable as α_1 , as well as, α_2 . Consequently, α_1 and α_2 are defined according to the following relation:

$$\alpha_1 = \alpha_2 = K \, \text{fldc2hs}((\varphi - 0.5), q) = \begin{cases} 0 & \text{if } |\varphi - 0.5| > q \\ \frac{K}{2q} \left[1 + \cos \left(\frac{\pi(\varphi - 0.5)}{q} \right) \right] & \text{if } |\varphi - 0.5| \leq q \end{cases} \quad (12)$$

Doing so, we have applied the maximum value to α_1 and α_2 at the interface where φ is zero and zero value at $|\varphi - 0.5| > q$. Given that φ varies from zero to one at the interface, q can take any value from between 0 and 0.5.

Maxwell equations were employed to calculate induced magnetic force on magnetic particles within the ferrofluid. For non-conducting media, Maxwell equations are expressed as follow:³⁸

$$\nabla \times \mathbf{H} = \mathbf{0} \quad (13)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (14)$$

where $\mathbf{H}$ is the magnetic field strength and $\mathbf{B}$ is the magnetic flux density. The relationship between the fields $\mathbf{H}$ and $\mathbf{B}$ for both magnetic and nonmagnetic media is:

$$\mathbf{B} = \begin{cases} \mu_0(\mathbf{M} + \mathbf{H}), & \text{if } \Omega_f \\ \mu_0\mathbf{H}, & \text{if } \Omega_n \end{cases} \quad (15)$$

where μ_0 is the permeability constant of the vacuum space with the value of $4\pi \times 10^{-7} \text{ N / A}^2$ and $\mathbf{M}$ denotes the magnetization of the ferrofluid. Langevin's magnetization function describes the magnetization behavior of the ferrofluid. According to this relation the magnetic nanoparticles have linear magnetization at low magnetic fields, which we have considered in this work for modeling the magnetization:³⁹

$$\mathbf{M}(\mathbf{H}) = \chi_{ff}\mathbf{H} = M_s (\cot(\gamma H) - 1/\gamma H) \mathbf{H} / H \quad (16)$$

where M_s shows saturation magnetization, γ is the Langevin parameter ($\gamma = 3\chi_0/M_s$, χ_0 is the initial susceptibility), $H = |\mathbf{H}|$ and χ_{ff} is magnetic susceptibility of the ferrofluid which is defined as:

$$\chi_{ff} = (M_s/H) (\cot(\gamma H) - 1/\gamma H) \quad (17)$$

The flux density inside the ferrofluid can be expressed as $\mathbf{B} = \mu_0(1 + \chi)\mathbf{H} = \mu\mathbf{H}$. Introducing the magnetic scalar potential ψ that takes the form of $\mathbf{H} = -\nabla\psi$ yielding:^{35, 40}

$$\nabla \cdot ((1 + \chi)\nabla\psi) = 0 \quad (18)$$

The concentration gradient of the magnetic nanoparticles, results in a magnetic permeability gradient across the domain. Considering the magnetic potential equation (18), the variation of the magnetic permeability inside the domain results in a gradient of the magnetic potential and the local magnetic field within the domain, while the magnetic field far from permeability variations

(near surrounding media boundaries) remains uniform. The magnetic susceptibility on the entire computational domain is obtained based on the harmonic mean:⁴⁰

$$\frac{1}{1+\chi} = \frac{1-\varphi}{1+\chi_c} + \frac{\varphi}{1+\chi_d}, \quad (19)$$

where χ_c and χ_d indicate the susceptibility of the continuous and dispersed phases, respectively.

Considering a very small solubility of magnetic particles in the continuous phase and the very large value of K , the susceptibility of this phase is approximated as zero.⁴¹ Furthermore, because of the existence of two miscible phases and the concentration gradient inside the dispersed phase, the susceptibility of the dispersed phase was chosen to be a function of the magnetic particles concentration($\chi_d(c) = c\chi_{ff}$, χ_{ff} is the magnetic susceptibility of ferrofluid with $c=1$). The magnetic force in a uniform magnetic field and for a linearly magnetizable medium is expressed as follow:³⁸

$$\mathbf{F}_m = -\frac{1}{2}\mu_0 C_v |\mathbf{H}|^2 \nabla \chi, \quad (20)$$

where C_v is the volume concentration of the magnetic particles ($C_v = cC_{v0}$, C_{v0} is the initial volume concentration). Also, approximating zero value for the susceptibility of the continuous

phase, the gradient of the susceptibility is calculated as $\frac{\partial \chi}{\partial \varphi} \nabla \varphi + \frac{\partial \chi}{\partial \chi_d} \nabla \chi_d$. The first term expresses

the variation of the susceptibility on the droplet interface, and the second one demonstrates the variation of the susceptibility inside the droplet due to the magnetic particles concentration gradient in the associated regions. According to equation (9) for a uniform magnetic field, the magnetic force acts on the areas where the susceptibility gradient exists. In our model, the concentration gradient inside the droplet and the permeability discontinuity across the interface give rise to susceptibility gradient and subsequently magnetic force in these domains. The

200 magnetic potential at the surrounding media boundaries was determined as the boundary condition
 201 for solving equation (18) and obtaining the magnetic potential within the entire domain. The
 202 magnetic potential on the surrounding media boundaries is calculated as follows:^{35, 41}

$$203 \quad \mathbf{H} \cdot \mathbf{n} = -\frac{\partial \psi}{\partial \mathbf{n}}, \forall \mathbf{x} \in \Omega \quad (21)$$

204 The variation of the density and viscosity is taken into account by expressing them as functions
 205 of concentration and phase field:

$$206 \quad \rho_d = c\rho_{ff} + (1-c)\rho_m \quad (22)$$

$$207 \quad \nu_d = \nu_{ff} e^{R(1-c)} \quad (23)$$

$$208 \quad \rho = \phi\rho_d + (1-\phi)\rho_c \quad (24)$$

$$209 \quad \nu = \phi\nu_d + (1-\phi)\nu_c \quad (25)$$

210 Where ρ represents the density, ν the viscosity and indices c, d, m and ff stands for continuous
 211 phase, disperse phase, deionized water-glycerol mixture and ferrofluid respectively. Furthermore,
 212 R is expressed as $R = \ln(\nu_m / \nu_{ff})$

213 To evaluate the mixing performance, the mixing index parameter is employed which is expressed
 214 as:⁴²

$$215 \quad M_i = 1 - \frac{\int_A |c_i - c_d| dA}{\int_A |c_0 - c_d| dA} \quad (26)$$

216 where c_i is the normalized concentration of species based on the inlet concentration, c_d is the
 217 average normalized concentration of species in the droplet, c_0 is the initial normalized

concentration and the dA is the infinitesimal area of the droplet.” . c_0 can change from 0 to 1 corresponding to fully unmixed and mixed solutions, respectively.

B. Numerical implementation

The presented models are implemented with the Finite Element Method (FEM) based software COMSOL, which allows for solving partial differential equations in a fully coupled approach. The implicit fifth order backward differential formula (BDF) is employed for temporal discretization, which is integrated with the spatial discretized partial differential equations.⁴³ Then, the set of obtained nonlinear equations in each time step is linearized by Newton method.⁴⁴ We used the Segregated approach, which treats each physics sequentially (Fig. 1), to solve the multiphysics finite elements. In this approach, the results of the previously solved physics are used to evaluate the loads and material properties for the next physics. Thus, first, the fluid flow solution with variables such as velocity field, pressure, level set function and Reciprocal initial interface distance was evaluated in each time step using guessing an initial value for material distribution and variables. Subsequently, the concentration distribution was evaluated with the solution from fluid flow and an initial value for the magnetic field. Finally, with the fluid flow and the mass transport solution that had been just computed, the magnetic field was solved. PARDISO solver was utilized for direct solving of the linearized equations. Besides accuracy, this solver is well known to be memory efficient and a robust tool for parallel computations. Also, because of the fast factorization process in this solver, the overall required solution time is reduced compared to the other direct solvers.⁴⁵ Moreover, to have an accurate approximation of the curvature and to preserve the level set function and the shape of the interface, a reinitialization step was used that requires the equation to be solved for a few pseudo time steps for each actual time step. For Navier-Stokes and mass

conservation equations, P2+P1 elements were set which provides the second order basis for velocity field and the first order basis for pressure. Level set and Maxwell equations were also solved via the second order discretization. Furthermore, considering high Peclet number, linear elements were utilized for mass transport physic.⁴⁶ Crosswind diffusion and stream diffusion stabilizers were applied to mass transport, as well as, two-phase flow physics to achieve more robust and faster computational performance. These artificial diffusion terms eliminate nonphysical local oscillations and capture discontinuities, however using coarse mesh or having considerable heterogeneity in mesh distribution gives rise to a deflection from the exact solution. To minimize this deviation, highly dense and smoothed mesh (with a maximum size of 6 micrometers) was employed in the channel geometry of our model.⁴⁷ For capturing the interface movement, COMSOL implements a conservative level set that has been developed by Olsson and Kreiss.³⁴ The main advantage of the conservative level set method compared to the standard level set method is preserving of the original area even in the highly curved evolving surfaces.⁴⁸

Fig. 1 Flowchart showing the numerical procedure

III. RESULTS AND DISCUSSION

A. Validation

1. Effect of magnetic field on the formation of ferrofluid droplets

Our model consists of a magnetic field effect on ferrofluid in both miscible and immiscible phases.

Thus, the numerical model is first examined for the magnetic effect on ferrofluid droplets. To this

aim, we validated the three-dimensional (3D) formation of ferrofluid droplets exposed to a uniform

magnetic field reported by Liu et al.⁴⁰ They explored the droplet formation process under magnetic

field influence in a flow focusing configuration, both numerically and experimentally. Based on

these studies, the magnetic force was acting on the droplet interface due to the permeability

discontinuity. Consequently, in the presence of a magnetic field parallel to the ferrofluid flow

direction, the additional magnetic force pulled the ferrofluid forward, elongated its tip as well as, its throat and delayed droplet formation. Thereby, the droplets formed under the magnetic field have a larger volume compared to those formed in the absence of the magnetic field. The authors considered the Bond number and magnetic susceptibility as indicators of magnetic field influence on droplet formation, and illustrated the size and shape dependence of the droplet to these factors. Figs. 2 and 3 show the droplet generation process for two cases without and with a magnetic field, respectively. The results illustrate a good agreement between our results and Liu et al. study.⁴⁰ For the first and the second cases (without and with the magnetic field), the dimensionless volume of the generated droplets in our work are approximately 0.71 and 1.16, and that of Liu et al. study⁴⁰ are approximately 0.83 and 1.25, respectively.

FIG. 2 Ferrofluid droplet formation without the magnetic field ($Ca = 2.22 \times 10^{-3}$, $Re = 2.78 \times 10^{-4}$, $Q_2 = 10 \mu l / h$, $Q_1 = 5 \mu l / h$, $B_m = 0$, $\chi_0 = 8$), (a) present results (b) Liu et al.

study⁴⁰. Reproduced from J. Liu, Y. F. Yap, and N.-T. Nguyen, "Numerical study of the formation process of ferrofluid droplets," Phys. Fluids, 23, 072008 (2011), with the permission of AIP Publishing.

FIG. 3 Ferrofluid droplet formation with the uniform magnetic field ($Ca = 2.22 \times 10^{-3}$, $Re = 2.78 \times 10^{-4}$, $Q_2 = 10 \mu l / h$, $Q_1 = 5 \mu l / h$, $B_m = 0$, $\chi_0 = 8$), (a) present results (b) Liu et al. study⁴⁰. Reproduced from J. Liu, Y. F. Yap, and N.-T. Nguyen, "Numerical study of the formation process of ferrofluid droplets," Phys. Fluids, 23, 072008 (2011), with the permission of AIP Publishing.

2. Magnetic field effect on bulk flow mixing improvement

After validating the numerical model for magnetic field effect on the immiscible two-phase system the numerical model is tested for magnetofluidic mixing of two miscible phases. We tried to replicate the Zhu and Nguyen work³⁵ that experimentally and numerically investigated the mixing of ferrofluid inside a circular chamber. In this study, high Peclet number and a negligible diffusive

296 mixing led to a sharp concentration gradient across the interface, which induced a large
297 susceptibility gradient and consequently instability when a uniform magnetic field was applied.
298 The mixing was studied for both ferrofluid-core and ferrofluid-cladding cases. Mixing
299 enhancement occurred in two regimes: (i) low magnetic field regime, where magnetophoresis of
300 the magnetic nanoparticles improved diffusive mixing, and (ii) strong magnetic field regime,
301 which generates a bulk secondary flow and accelerates mixing due to magnetoconvection.
302 Moreover, the effect of parameters such as flow rate ratio, flow rate and viscosity on mixing
303 efficiency are investigated. In the numerical section of the Zhu and Nguyen study³⁵ variation of
304 mixing efficiency over a range of magnetic field strength was verified. Water-based ferrofluid and
305 a mixture of DI water and glycerol were used as miscible fluids. Flow rates of 0.5 ml/h were
306 considered for both fluids. Also, the viscosity ratio of diamagnetic to ferrofluid was fixed at 0.5.
307 Subsequently, we compared our results with those obtained by Zhu and Nguyen study³⁵ in Fig. 4.
308 Our results show an acceptable agreement with Zhu and Nguyen study. According to our results,
309 the mixing index for ferrofluid core is approximately 0.75 and that for the ferrofluid cladding
310 is approximately 0.86. Consistently, Zhu and Nguyen obtained the values of 0.74 and 0.9 for
311 ferrofluid core and the ferrofluid cladding, respectively.

FIG. 4 Concentration contour of (a) ferrofluid-cladding configuration without magnetic field (b) ferrofluid-core configuration without magnetic field, (c) ferrofluid-cladding configuration with the magnetic field and (d) ferrofluid-core configuration with the magnetic field. (i) present results (ii) Zhu and Nguyen study³⁵. Reproduced from G.-P. Zhu, and N.-T. Nguyen, "Rapid magnetofluidic mixing in a uniform magnetic field," *Lab on a Chip* 12, 4772 (2012), with the permission of Royal Society of Chemistry Publishing.

B. Mixing enhancement in droplet-based micro magnetofluidics

1. Materials and Methods

Fig. 5 illustrates the schematic of our proposed model. The main simulation domains include a disperse-phase flow containing two miscible fluids, a continuous-phase flow, and surrounding media. Droplets are generated and merged in a double T-junction device with a straight main channel and two horizontally symmetric side channels. Considering the shallow microchannels (with 50 depths and the aspect ratio of 3), two-dimensional (2D) model is employed for numerical simulation. The two miscible disperse-phase fluids flow through the side channels (water-based ferrofluid from the lower channel and a diamagnetic glycerol-water mixture from the upper channel) while the continuous fluid (oil), flows through the main channel. Considering water-based ferrofluid, the solubility of magnetic nanoparticles inside the oil is near zero, which results

331 in a concentration jump across the ferrofluid-oil interface. Besides, merging of two miscible phases
 332 establishes additional concentration gradient inside the droplet. After applying a uniform magnetic
 333 field, the existing concentration gradients creates an extra magnetic force. To provide
 334 experimentally replicable results, the materials properties were extracted from the similar
 335 experimental studies. The magnetization saturation of the ferrofluid is 32.5 mT, its density is
 336 $\rho_{ff} = 1.1 \times 10^3 \text{ kg m}^{-3}$ and its viscosity is $\nu_{ff} = 5 \text{ mPa} \cdot \text{s}$. The initial volumetric concentration and
 337 the initial susceptibility of the ferrofluid are set as 2% and $\chi_{ff} = 0.36$, respectively. The
 338 diamagnetic mixture is considered to be made of 65.6 wt% deionized water and 34.4 wt% glycerol.
 339 Consequently, the mixture has the viscosity and the density of $\nu_m = 2.5 \text{ mPa} \cdot \text{s}$ and
 340 $\rho_m = 1.09 \times 10^3 \text{ kg m}^{-3}$, respectively.³⁵ The viscosity and density of the oil are $\rho_o = 960 \text{ kg m}^{-3}$ and
 341 $\nu_o = 96 \text{ mPa} \cdot \text{s}$. The Marangoni effect is ignored and a constant value of $\sigma = 12 \text{ mN/m}$ is used
 342 for both oil-ferrofluid and oil-mixture interfacial tensions.^{40, 49, 50} Given that the two miscible fluids
 343 have very close properties, it would be a valid assumption to ignore the Marangoni effect in the
 344 solution as frequently being assumed in previous works on mixing inside droplets.^{28, 42} The
 345 diffusion coefficients of magnetic nanoparticles into the water-glycerol mixture, as well as, oil are
 346 obtained from Einstein's model as $D = k_b T / 3\pi\eta d_p$, where D shows diffusion coefficient, k_b
 347 Boltzmann constant, T absolute temperature and d_{mp} the magnetic particles diameter. Considering
 348 the temperature of 300 K and $10 \times 10^{-9} \text{ m}$ particles diameter, the diffusion coefficients of magnetic
 349 particles into the mixture and the oil are calculated as 1.76×10^{-11} and 4.58×10^{-13} , respectively.
 350 To describe the dynamic of a two-phase flow, as well as the influence of the magnetic forces on

the inhomogeneous ferrofluid, we utilized the coupled systems of Maxwell equations, advection-diffusion equation, incompressible Navier–Stokes equation and the Young–Laplace equation.³⁹

FIG. 5 Schematic of the droplet-based micromagnetofluidic for mixing enhancement inside the microdroplets.

The effective dimensionless numbers in this study are Reynolds, Peclet and Capillary numbers. Reynolds number is the ratio of the inertia force to the viscous force. This number determines the flow regime inside the channel. Because of the tiny microchannels, the Reynolds number all over this study is very smaller than one, so the flow regime is laminar. Peclet number shows the ratio of convective mass transport to diffusive mass transport. For high Peclet numbers, a substantial proportion of the mass transport is carried out by convection. Also, Capillary number plays a pivotal role in droplet generation regime. This number shows the ratio of the viscous forces to the interfacial tension. For double T-junction devices, previous studies have classified droplet formation regimes according to the Capillary number, as well as, dispersed phase volume fraction to four subcategories: merging, alternating, small droplets, and laminar regimes. According to these studies, for a constant value of the dispersed phase volume fraction, as the Capillary number increases the droplet formation regime changes from merging to laminar.^{51, 52}

368 In the present study, we also explore the influence of key parameters such as magnetic field
 369 strength, droplets mean velocity and droplets size on mixing enhancement, systematically. To
 370 verify the effect of the magnetic field on mixing behavior, a magnetic field varying from 10 mT
 371 to 90 mT is exploited in the simulation. For this case, the flow rate of the oil is set as 0.09 ml/h,
 372 and the flow rates of each of dispersed fluids (ferrofluid and the mixture) is 0.009 ml/h. The
 373 corresponding Reynolds number ($Re = \rho_c u_c L / \eta_c$, L is the width of the main channel), Capillary
 374 number ($Ca = \eta_c u_c / \sigma$) and Peclet number ($Pe = u_s l_s / D_{mp}$, u_s is the velocity of the slug, l_s is the
 375 length of the slug and D_{mp} is diffusion coefficient of the magnetic particle to the diamagnetic
 376 mixture) are $Re = 5 \times 10^{-3}$, $Ca = 2.67 \times 10^{-2}$, $Pe = 6.57 \times 10^4$.

377 The other verified parameter is the mean velocity of droplets in the main channel. We kept the
 378 aspect ratio of the flow rates fixed ($Q_r = Q_c / Q_d = 3.33$, $Q_d = Q_{ff} + Q_m$) and altered their
 379 magnitudes, so that the flow rates of the continuous and dispersed phases vary from 0.096 to 0.144
 380 ml/h and 0.0288 to 0.0432 ml/h, respectively ($1.0 \leq Q_v = Q / Q_0 \leq 1.5$, Q_v is the dimensionless
 381 value of flow rate that is obtained by dividing the flow rate to the initial flow rate). The
 382 corresponding ranges of the Reynolds number are from 5.33×10^{-3} to 8.0×10^{-3} , the ranges of the
 383 Capillary number are from 2.84×10^{-2} to 4.27×10^{-2} and the ranges of the Peclet number are from
 384 5.93×10^4 to 8.43×10^4 .

385 Finally, the effect of the droplet size on mixing is investigated by shifting the dispersed phase
 386 flowrate from 0.018 ml/h to 0.09 ml/h and maintaining the continuous phase flowrate constant at
 387 0.12 ml/h. Accordingly, the corresponding Reynolds number and Capillary number are 6.67×10^{-3}
 388 and 3.56×10^{-2} , respectively. Also, the ranges of the Peclet number is from 5.12×10^4 to 1.3×10^5

The above-mentioned circumstances, suggest laminar flow because of the low Reynold numbers, small diffusion because of the high Peclet numbers and merging regime of droplet formation due to the low Capillary number.

2. Mesh convergence

In all the geometries, three-dimensional tetrahedral grids were used for meshing. Mesh independency was examined by three case studies (19,266; 33,052 and 47,264 number of grids). In the channel domain, the mesh was highly smoothed in all cases with a maximum element growth rate of 1.08. Fig. 6 (a) and (b) show the yielded droplet shapes and particles concentration distribution for all these cases. Negligible changes were observed when grids number went beyond 33,052. In the present study, 47,264 elements were used for meshing.

FIG. 6 Mesh convergence study (a) droplet shapes for a different number of grids (b) particles concentration distribution for (i) 19266 grids (ii) 33052 grids (iii) 47264 grids ($Q_c = 0.09 \text{ ml} / h$, $Q_{ff} = Q_m = 0.009 \text{ ml} / h$, $\mathbf{B} = 0 \text{ mT}$).

3. Droplet formation in the double T-junction device

As discussed previously, a double T-junction configuration is considered for droplet forming and merging.^{51, 52} This configuration operates in four different regimes, which are characterized by the capillary number and dispersed phase volume fraction. The present study implements small capillary number and small volume fraction of the dispersed phase. Thus, merging of dispersed phases occurs at the very beginning of the main channel. However, other scenarios for droplet merging and mixing are possible. For instance, droplet merging and mixing can be realized in an alternative regime by employing a suitable magnetic field configuration.

The mechanism of the droplet formation is such that in the early growth stage of the dispersed phases, the bulged part of the droplet grows both horizontally and vertically. Meanwhile, the gap between two dispersed phases reduces, leading to a narrower film of the immiscible phase. Finally, the film ruptures and the two miscible phases coalesce. According to the previous studies, the small values of the viscosities of the dispersed phases improve surface mobility and make merging easier. Also, large values of the interfacial tensions speed up coalescing.⁵¹ After coalescence, the main channel is blocked with dispersed phases. The blockage increases the pressure upstream of the cross junction. The growth of the disperse phase in the channel continuously enlarges the pressure gradient across the droplet. Finally, the pressure gradient overcomes the pressure inside the dispersed phase and squeezes the interface. The generated droplet is confined by channel walls and adapts a plug shape^{53, 54}. Any increase of the flow rate of the continuous phase amplifies the pressure gradient in the channel and accelerates the droplet formation. After a threshold value, increasing of the continuous phase flow rate makes the dispersed phases unable to rupture the film and droplet generation regime changes.

Our results show a slight delay in ferrofluid detachment compared to the diamagnetic mixture detachment (Fig. 7), which is consistent with previous researches offering that an increase in dispersed phase viscosity, elongates the neck and postpones the detachment.⁵¹ This delay in detachment contributes to the fluids distribution inside the droplet, right after the formation. Particles concentration contours during droplet formation process without magnetic field and under a uniform magnetic field of 90 mT strength are demonstrated in Figs. 7(a) and 7(b) respectively. It is noteworthy that the detachment of the mixture fluid is at the same time for both cases, while the ferrofluid with magnetic field detaches in a shorter time compared to without magnetic field. This issue can be attributed to the internal hydrodynamic of the droplet. Under the

influence of the magnetic field, the ferrofluid rises at the center rear part of the droplet, which results in drainage of the ferrofluid neck and acceleration of the ferrofluid detachment.

FIG. 7 concentration contour during droplet formation process (a) without magnetic field (b) subjected to a magnetic field with 90 mT strength.

4. Mixing efficiency inside droplets under different magnetic field strengths

Figs. 8 and 9 illustrates th mixing behavior inside moving droplets for different values of magnetic field strengths. According to these results, in the early stages of increasing the magnetic field, the mixing efficiency inside droplets increases rapidly. The efficiency growth then diminishes gradually, and after a specific value, any increase of the magnetic field strength has an adverse effect on mixing efficiency. In the absence of the magnetic field, the flow topology inside the droplet is influenced by parameters such as fluids properties, channel geometry, droplet size, and droplet velocity.^{55,56} For plug shape droplets, a thin film of the continuous phase is formed between the droplet and the channel wall which exerts shear forces on droplet sides. Under these circumstances, the difference between droplet velocity and mean velocity in the channel results in

the emergence of horizontally symmetrical internal recirculation in the droplet.⁵⁷ Considering the lower half of the droplet, during droplet movement inside the channel a clockwise vortex develops in the droplet flanks that accompanied two weaker counter-clockwise vortices in the rear and front parts (Fig. 10 (a-i) and (b-i)). This pattern of the internal flows is maintained throughout the droplet traveling in a straight channel.

Droplets exposed to the uniform magnetic field experience magnetic force in two ways. First, because of the distinct solubility of magnetic particles in two immiscible phases and their concentration difference, the magnetic force acts at their interface and elongates the droplet in line with the magnetic field. Moreover, once the miscible phases merge, a sharp concentration gradient exists at their interface. The established magnetic force due to the susceptibility gradient within the droplet has the most impact on the internal flow patterns. After applying the magnetic field, depending on the strength of the field, the existing magnetic susceptibility gradient at the interface of miscible phases gives rise to two different mixing behaviors, Figs. 6(b-e).

At low magnetic fields, the magnetophoresis improves nanoparticles migration from the high concentration to the low concentration regions. Under this condition, the dominant mode of particles transport is diffusion. On the other hand, If the magnetic field becomes large enough, the magnetic force disturbs the symmetry of the internal droplet flows and produces secondary flows. That way, as long as the susceptibility gradient parallel to the magnetic field is sufficiently large, the number and size of vortices inside the droplets are constantly changing. Here the particles transportation is mainly realized through the bulk flow convection, which leads to a considerable enhancement of mixing.³⁵ After droplet formation, most of the particles are trapped within the lower half recirculation zones of the droplet, which are hydrodynamically isolated from the upper ones. Weak magnetic fields only improve diffusive behaviors of the particles, so they have a small

influence on mixing improvement, Fig. 8(b) and 9. With augmenting the magnetic field strength, it is possible to create secondary flows in the regions with sharp concentration gradients; however, once the gradient is reduced, the magnetic force is attenuated and unable to perturb the symmetry of the recirculation flows any longer, Fig. 8(c).

Increasing the magnetic field strength enhances the particles convection in the droplet. Because of the nearly complete predominance of the magnetic force to other driving forces, particles are transported in the magnetic field direction swiftly, and distributed at the rear center part of the droplet vertically, Fig. 8 (d) and (e). Intensifying of the magnetic field accelerates particles convection and increases the volume of the transported particles. After homogenization of particles in the same direction of the magnetic field and reduction of the magnetic force, the vortices inside the droplet turn to its symmetrical configuration (Fig. 10 (a-ii), $t=264$ ms). In this instance, the droplet middle vortices are smaller than that of the zero magnetic field case. However, these vortices gradually grow as the droplet moves within the channel and particles diffuse toward the droplet leading edge. During this process, exerting shear forces proceeded by droplet movement tend to enlarge the vortices in the droplet flanks, whereas particles under the influence of the uniform magnetic field resist deviation from the homogenized state.

As the stronger magnetic force is employed, the effect of this resistance is more pronounced. As such, the strong magnetic force slows down the variation of the middle part vortices and reduces the homogenization, Fig. 8(e) and Fig. (9). Fig. (9) clearly shows that mixing performance in droplets exposed to magnetic field consists of two steps. At the beginning of the droplet movement in the channel, the variation of the efficiency with the time has a steep slope that increases with increasing the magnitude of the magnetic field. This behavior is due to the massive particle convection by magnetic forces when a sharp susceptibility gradient exists in the droplet. After

dropping of the gradient in magnetic field direction, the main driving force of the mass transport is diffusion which acts much slower than convective mass transport, so the slope declines significantly.

Figure 10 shows the streamlines of internal flows in the droplet frame of reference. The figure is related to the initial steps of the droplet movement within the channel for two cases of without magnetic field and in a 90-mT magnetic field. As observed in Fig. 10 (a-i), for the case of zero magnetic field, at the very beginning after the droplet formation, the recirculation patterns and particles distribution inside the droplet is asymmetrical. The main reason for the imbalance is the difference in the fluids properties, which affect the droplet formation process. However, as discussed above, shortly after the droplet movement in the channel, the symmetrical pattern of the recirculation flows appears inside the droplet. At the initial steps of applying the magnetic field, a large vortex developed in the center of the droplet due to the intense magnetic force, Fig. 10 (a-ii) ($t=115$ ms). The vortex transports a remarkable volume of particles vertically and moves them toward the rear part of the droplet, Fig. 10 (a-ii) ($t=115$ -154 ms). Meanwhile, new vortices emerge in the middle of the droplet. Then, the large vortex divides into new vortices, and the internal flows advance toward their symmetrical shapes. After the formation of the symmetrical vortices, the majority of the particles are isolated at the middle and rear vortices. These particles transport to the droplet head through the diffusion, as well as, expansion of the middle vortices.

FIG. 8 Nanoparticles concentration distribution in micro droplets under influence of the magnetic fields with (a) 0 mT (b) 10 mT (c) 30 mT (d) 60 mT and (e) 90 mT strengths ($Q_{ff} = Q_m = 0.009 \text{ ml} / h$, $Q_c = 0.09 \text{ ml} / h$).

FIG. 9 Mixing efficiency in droplet versus time for different values of the magnetic field strengths ($Q_{ff} = Q_m = 0.009 \text{ ml/h}$, $Q_c = 0.09 \text{ ml/h}$).

FIG. 10 Mixing performance of droplet at initial steps of droplet moving in microchannel (a) relative velocities and streamlines in the droplet frame of the reference, (b) nanoparticles concentration distribution inside the droplets for (i) without magnetic field, and (ii) exposed to a magnetic field with 90mT strength ($Q_{ff} = Q_m = 0.009 \text{ ml/h}$, $Q_c = 0.09 \text{ ml/h}$).

5. Mixing efficiency inside droplets with different mean velocities

To evaluate the influence of the droplet velocities on the mixing efficiency, we kept the aspect ratio of the flowrates fixed ($Q_r = Q_c / Q_d = 3.33$) and varied their magnitudes (

535 $1.0 \leq Q_v = Q/Q_0 \leq 1.5$). Figs. 11 and 12 illustrate the mixing process and efficiency within the
 536 microdroplets for different values of Q_v . At low mean velocities, the magnetic force rapidly
 537 distorts the vortices and accumulates a large volume of the particles at the rear center of the droplet,
 538 Fig. 11(a). Increasing the droplets velocity intensifies viscous force and accordingly strengthens
 539 vortices inside the droplets. As a result, the boosted vortices resist to change under the same
 540 magnetic force (peculiarly middle vortices, which have the most strength). Subsequently, the
 541 magnetic force develops the recirculation zones containing nanoparticles towards the weaker
 542 vortex at the upper front part of the droplet. The magnetic force pulls the particles upward and
 543 shrinks the upper middle vortex. Because of the relatively high strength, the shrinkage of the upper
 544 middle vortex is insignificant, and a part of the particles move toward the droplet tip. At the
 545 intermediate conditions, balancing between magnetic forces and shear forces caused by droplet
 546 movement in the channel leads to an approximately uniform particles distribution all over the
 547 droplet and enhances mixing, remarkably, so that mixing efficiency can reach more than 94%,
 548 Figs. 11(b) and 12. Further increasing the droplet velocity prevents the deformation of the upper
 549 middle vortex and makes particles convection to this region difficult. Thus, most of the particles
 550 remain confined in the lower vortices or move to the droplet tip. This status causes a heterogeneity
 551 in particles distribution, which exacerbates with increasing droplet velocity, Figs. 11(c-e) and 12.

FIG. 11 Nanoparticles concentration distribution in microdroplets with various average velocities (a) $Q_v = 1$, (b) $Q_v = 1.125$, (c) $Q_v = 1.25$, (d) $Q_v = 1.375$ and (e) $Q_v = 1.5$ ($\mathbf{B} = 60 \text{ mT}$, $0.096 \leq Q_c \leq 0.144 \text{ ml/h}$, $0.096 \leq Q_c \leq 0.144 \text{ ml/h}$).

558

559 **FIG. 12** Mixing efficiency in droplet versus time for different values of the average droplet
 560 velocities ($\mathbf{B} = 60 \text{ mT}$, $0.096 \leq Q_c \leq 0.144 \text{ ml/h}$, $0.096 \leq Q_c \leq 0.144 \text{ ml/h}$).

561 Figure 13(a) demonstrates the streamlines and velocity contours inside droplets with different
 562 mean velocities, where the center-to-center distance between the droplet and the cross junction is
 563 nearly 250 micrometers. Also, the related concentration contours are represented in Fig. 13(b),
 564 which clearly shows that increasing droplet velocity hampers upper middle vortex deformation,
 565 and causes convection of particles towards the droplet tip.

FIG. 13 Mixing performance of droplets with various droplet average velocities and 250 micrometers center to center distance from the cross junction, (a) relative velocities and streamlines in the droplet frame of the reference, (b) nanoparticles concentration distribution inside the droplets ($B = 60 \text{ mT}$, $0.096 \leq Q_c \leq 0.144 \text{ ml/h}$, $0.096 \leq Q_c \leq 0.144 \text{ ml/h}$).

6. Mixing efficiency inside droplets with different volumes

Another influencing factor on mixing efficiency is the droplet size. To verify the influence of droplet volume on mixing efficiency, we used different values of dispersed phase flow rates. For large flow rates of the dispersed phase, volume and speed of the droplets increases, and their distance gets smaller. Under these circumstances, the middle part vortices of droplets become large and strong, while other vortices (rear and front part vortices) change slightly (Fig. 16). According to the previous arguments, as the vortices strengths increase, more energy is required to deform them. Hence, as the droplets are getting bigger, the magnetic field has a weaker influence on the flank vortices. As a result, the magnetic field steers particles toward weaker vortices and their boundaries. The decrease of the concentration gradient inside the droplets progressively brings the vortices shapes closer to their symmetrical states. Meanwhile, the upper middle vortex is developing downward and takes a part of the particles from this region. As initial changes of vortices become larger, more particles get stuck in upper middle vortex following their

development. These particles follow the rotational flow of the vortex, which improves mixing inside the droplets. In small droplets, mass transport between these vortices takes place more conveniently because of the narrower boundary between droplet middle and tip vortices, Figs. 14 and 16.

FIG. 14 Nanoparticles concentration distribution in microdroplets of different sizes (a) $Q_r = 6.67$, (b) $Q_r = 4$, (c) $Q_r = 2$ and (d) $Q_r = 1.33$ ($\mathbf{B} = 60 \text{ mT}$, $Q_c = 0.12 \text{ ml} / h$, $0.018 \leq Q_d \leq 0.09 \text{ ml} / h$).

Fig. 15 Mixing efficiency in droplet versus time for different values of the droplet sizes ($\mathbf{B} = 60 \text{ mT}$, $Q_c = 0.12 \text{ ml/h}$, $0.018 \leq Q_d \leq 0.09 \text{ ml/h}$).

FIG. 16 Mixing performance of droplets with various sizes and 300 micrometers center to center distance from the cross junction, (a) relative velocities and streamlines in the droplet frame of the reference, (b) nanoparticles concentration distribution inside the droplets ($\mathbf{B} = 60 \text{ mT}$, $Q_c = 0.12 \text{ ml/h}$, $0.018 \leq Q_d \leq 0.09 \text{ ml/h}$).

7. Evaluation of mixing in a combined diagram

For more insight into the mixing behavior inside the droplets, three different parameters were employed as indicators for droplet velocity, droplet size and the magnetic field strength:

$$Ls_av = (L_d - L_{d_min}) / (L_{d_max} - L_{d_min}) \quad (27)$$

$$Ca_av = (Ca_d - Ca_{d_min}) / (Ca_{d_max} - Ca_{d_min}) \quad (28)$$

$$Bm_av = (B_m - B_{m_min}) / (B_{m_max} - B_{m_min}) \quad (29)$$

where L_d is the droplet length within the channel, Ca_d is the dispersed phase Capillary number B_m is the magnetic Bond number and max and min stand for the maximum and minimum value of the related parameters in a group of studied items (cases). The reason for the definition of the parameters based on their maximum and minimum values is obtaining a unit range of variations (between zero and one) which is a convenient way for showing all these parameters on a diagram. The Ca_d and B_m can be calculated by:

$$Ca_d = \bar{\eta}_d U_d / \sigma \quad (30)$$

$$B_m = \mu_0 R_0 H^2 / \sigma \quad (31)$$

where $\bar{\eta}_d = 3.75 \text{ mPa} \cdot \text{s}$ is the average viscosity inside the droplet, U_d is the droplet velocity and R_0 is the droplet radius for without deformation state.

Fig. 17 represents the combined diagram, which evaluates the variation of the mixing index with regard to the three parameters (Ls_av , Ca_av , Bm_av), concurrently. According to this figure, for items 1 to 5 where Ls_av and Ca_av are almost constant, there is a specific value for Bm_av where the mixing index is maximized (item 4). For items 6 to 10, Bm_av is nearly

fixed, Ls_{av} changes smoothly and Ca_{av} shifts significantly. Also for this case, the value of MI peaks where the ratio of the Bm_{av} to Ca_{av} is a certain value (item 7). The comparison of two items 4 and 7 illustrates that higher Ca_{av} and relatively smaller Ls_{av} can result in larger mixing efficiency. Verifying items 10 to 14 shows the worsening of the mixing with striking growth of Ls_{av} and Ca_{av} , while Bm_{av} is near constant. These observations support our previous discussion that optimized mixing occurs for a given ratio of the magnetic force to the shear force. And using smaller drops has a positive effect in mixing enhancement. Also based on the diagram synchronized increase of the magnetic and the shear forces improves mixing.

FIG. 17 Combined diagram for simultaneous evaluation of mixing under influence of different parameters

IV. CONCLUSION

639 This work demonstrates active mixing of ferrofluid with a diamagnetic glycerol-water mixture in
640 microdroplets under a uniform magnetic field. Low Reynolds and Capillary numbers provide
641 laminar flow and merging droplet formation regimes, respectively, while high Peclet number
642 offers negligible diffusion. Uniform magnetic field induces a magnetic force on both ferrofluid-oil
643 and ferrofluid-diamagnetic mixture interfaces, where mismatched magnetic susceptibility exists.
644 The magnetic force exerting on the droplet boundary leads to droplet deformation, and that
645 applying on miscible phases interface destroys the symmetry of the flow patterns in the droplet.

646 The influence of three factors including, magnetic force, droplet velocity and droplet size on
647 mixing efficiency was examined. For the first factor, results showed that a strong magnetic force
648 rapidly redistributes particles and accumulates them in the middle and rear vortices. However,
649 under a low magnetic field strength, the perturbations caused by magnetic force are very poor, and
650 subsequently, particles transportation between two halves of the droplet occurs mainly through the
651 diffusion. Additionally, it was seen that the increase of droplet velocity and size have a negative
652 impact on the response of the particles to the magnetic field as it reinforces shear forces and
653 vortices strength inside the droplet. Particles convection inside the droplet is regulated by the
654 interaction between the magnetic force and shear force that proceed from the droplet movement
655 within the channel. Our results indicated that to attain optimized mixing a balance between the
656 magnetic force and shear force should be realized. The dominant magnetic force vigorously
657 manipulates vortices and in a very short time homogenizes particles in line with the magnetic field
658 at droplet flanks and rear part while droplet tip becomes nearly empty from particles. Then vortices
659 evolve to their symmetrical configuration, and mass transport to the droplet tip mostly occurs
660 through the very slow mechanism of diffusion. On the other hand, powerful shear force excludes
661 magnetic force from developing inhomogeneity in the recirculation zones. In this case, the

magnetic field is only able to drag a minor part of particles toward the weaker vortices in the droplet tip or boundaries between vortices and significant amounts of particles remain in the lower half of the droplet. At intermediate levels, gentle changes in vortices by the magnetic field, Spreads the particles uniformly across the droplet. The mixing efficiency of 94% was demonstrated for this condition. Also, it was observed that smaller droplets are better candidates for droplet mixing. Hence, the thinner diffusion barriers between their vortices make the mass exchange between inner vortices easier. From a practical point of view, controlling the mixing with adjustment of the flowrates through syringe pumps or regulating the magnetic field through a customized electromagnet is more affordable than other approaches. Nevertheless, other strategies for controlling mixing are possible. Employing ferrofluids with different properties (nanoparticles concentration, magnetic susceptibility, etc.) could be useful in tuning the magnetic force and flow characteristics. Finally, to speed up the mixing process, one can concurrently increase the magnetic force and the droplet speed until the formation regime changes to alternating one, in which different kinds of magnetic configuration can be employed to accomplish droplet merging and mixing in the microchannel.

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