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Magnetic Nanoparticles as Controlling Agents of Chain Structures in a Rotating Magnetic Field

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Chain formation in magnetic fluid has been observed under the influence of a rotating magnetic field. The influence on the chain flexibility and its rupture was studied by varying the frequency of rotation (1-5 Hz) of the magnetic field of a fixed magnitude (50 Gauss). Micrometer sized Fe_3O_4 particles and non-magnetic expancel spheres of fixed concentration were later suspended in the magnetic fluid separately and their effect on the chain rotation dynamics was studied. It was observed that the critical frequency for the chain breakage was higher in the presence of larger magnetic particles compared to magnetic fluid alone. Non-magnetic particles formed chain structures in the presence of a static field but did not show any response to the rotation of the magnetic field. The established theory of magnetic chain formation was used to study and discuss the results by comparing the magnetic forces and viscous forces. The study may be useful for controlling chain length and flexibility in microfluidics.

Keywords: Magnetic fluid, Nanoparticles, Magnetic field.

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1. INTRODUCTION

An externally applied magnetic field is an effective tool for controlling magnetic particles in superparamagnetic colloids. Hence, investigation of colloidal aggregation under the influence of uniform/non-uniform external magnetic force is the quest for both practical and fundamental reasons. Induced structuration in these delicate self-assembled nanostructures in the presence of inhibited external magnetic field has created massive opportunities in the exploration of novel magnetic materials for many applications in together with fields as diverse as biotechnology or waste removal [1]. The magnetophoretic effect of a non-uniform magnetic field enables the motion of magnetic nanoparticles towards a stronger magnetic field which is exploited in magnetic separation at a great extent [2]. In biological applications like protein isolation, cell separation, drug delivery, and biocatalysis, superparamagnetic colloids can be functionalized with appropriate chemical groups to bind with specific targets and can be removed using magnetic field gradients [3]. Observed density gradient inside magnetic fluid enables levitation of non-magnetic materials in it which provides several contact-free manipulation methodologies in the broad areas of chemistry, materials science, and biochemistry [4].

The formation of self-assembled chain structures under the influence of a uniform magnetic field is performed as magnetic devices in micro-magnetofluidics and successfully operated as artificial swimmers or active fluid mixers [5]. Several recent, theoretical studies have focused on the study of the kinetics and equilibrium of chain growth under an external homogenous and constant magnetic field [6].

The superparamagnetic particles of ferrofluid be likely to align in the direction of external magnetic field [7] but due to a finite temperature of the ferrofluid, the nanoparticles' thermal agitation competes with the applied magnetization force. Experimental studies of equilibrium state of chain formation of ferrofluids in a uniform/non uniform fields were done [8-14].

Experimental and theoretical studies on the effect of rotating magnetic field on linear chain formations for different particles has been done before [15-17]. The elongated chains can be used as magnetic stirrers [18, 19] or to realize biomimetic structures such as artificial cilia [20, 21] and the controlled motion of such structures have potential applications in micro/nanofluidics. The reliability of such structures in these applications demands a detailed study of their strength and flexibility [22]. The effect of presence of non-magnetic particles on the chain formation and their properties needs to be studied. This applies to the vast variety of magnetic fluids and other colloidal systems.

Here, the experiments carried out to study the chain formation, their flexibility and strength under the influence of a rotating magnetic field has been discussed. First the effect of rotation of magnetic field on the chain formation in kerosene based magnetic fluid was studied. The same experiment was repeated with i) micrometer sized flake shaped magnetic particles and ii) micrometer sized spherical non-magnetic particles suspended in magnetic fluid. The effect of presence of these magnetic as well as non-magnetic particles in magnetic fluid were studied in terms of chain formation and rotation.

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2. EXPERIMENTAL

Kerosene based ferrofluid utilized in the present work was synthesized using well known chemical co precipitation technique and elaborative discussion regarding the same has been given in our earlier published studies [23, 24]. The primary structural and magnetic parameters of the used ferrofluid have been reiterated here for reference information. The hydrodynamic particle size was measured using by dynamic light scattering (ZS-90, Malvern Zeta Sizer) which was found 13 nm (Fig. 1). Further the particle size distribution has been also confirmed by TEM measurements employed in imaging mode [24]. The obtained value of saturation magnetization field (Ms) was 25 Gauss (using search coil method), diameter (Dm) of the magnetic nanoparticles was 13 nm and domain magnetization (Md) is 320 emu/cc. The rheological parameters like density and zero field viscosity of the fluid were measured using Magneto Rheometer (Anton Paar MCR302) at 30 °C and subsequently the obtain parameters are 0.8919 gm/cc and 2 cP.

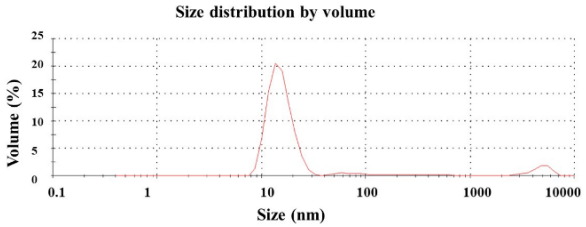

Fig. 1 – Hydrodynamic particles size of 15 nm obtained from DLS measurement at 25 °C

The aim of the present study was to analyze chain structures under the influence of a uniform rotating magnetic field at different frequencies. For this, an in-house arrangement was made for the application of an external magnetic field parallel (in plane) to the substrate which could be rotated in the plane of the substrate.

Fig. 2 shows schematic diagram of the assembled set up. Two pairs of Helmholtz coils were prepared with a fixed power supply, giving a uniform magnetic field of 50 Gauss in the central region. The power supply was passed through a function generator which generated separate sine wave signals for the two coil pairs. A phase lag of 90 degrees was applied between the input signals of the two coils, creating an effective rotating magnetic with a frequency range 0-5 Hz. During the experiment, ferrofluid drop of ≈ 50 μL was placed on a clean glass substrate and covered by a cover slip to prevent evaporation. To observe and record the dynamics of particle chain formation, the coil setup was integrated with an optical microscope attached with a CCD camera to the eye piece of the microscope.

The chain rotation dynamics has been observed in three different kind of fluid samples. Initially, (i) magnetic fluid of 1 % volume fraction was subjected to rotating magnetic field and dynamics observed under microscope. Later as separate experiments, ferrofluid sample mixed with (ii) micron sized flake shaped iron oxide particles (~ 100 μm, Tata Steel) of 0.1 % volume fraction and (iii) non-magnetic expancel microspheres of 0.1 % volume fraction were observed under similar conditions of rotating magnetic field. Since the study was intended to understand only the influence of frequency, the volume fraction of magnetic fluid (1 %), flake shaped particles (0.1 %), expancel microspheres (0.1 %) were not varied and magnetic field intensity was also kept constant (50G) throughout the experiments. The response of chains for different frequencies (between 1-5 Hz) in the rotating magnetic fields were observed/photographed and length of chains were measured using ImageJ software.

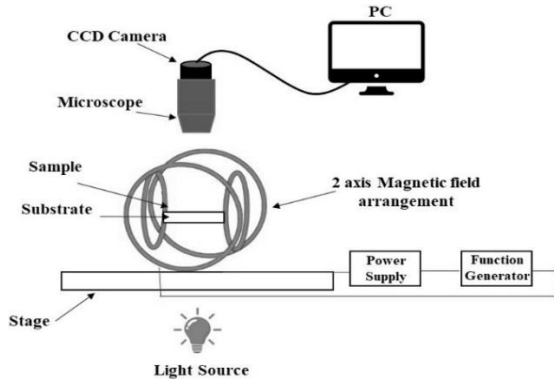

Fig. 2 – Schematic diagram of external magnetic field applied parallel to the substrate. After the formation of chains, the magnetic field was rotated in the plane of the substrate

3. RESULTS AND DISCUSSION

After optimization of the direction of easy axis of magnetization of the chains along that of the applied field, magnetic fluid chains then subjected to the rotational magnetic field. Fig. 3 and Fig. 4 show the microscopic images of magnetic fluid chains at different frequencies. During rotation, the chains seemed rigid at lower frequency but with increasing frequency, a bending in the chains was observed.

Chain formation occurs due to dipole-dipole attraction between two neighboring particles. The magnitude of a particle's magnetic dipole moment under the influence of an external magnetic field is expressed as

$$\mu = V\chi\mu_0 H_0 \tag{1}$$

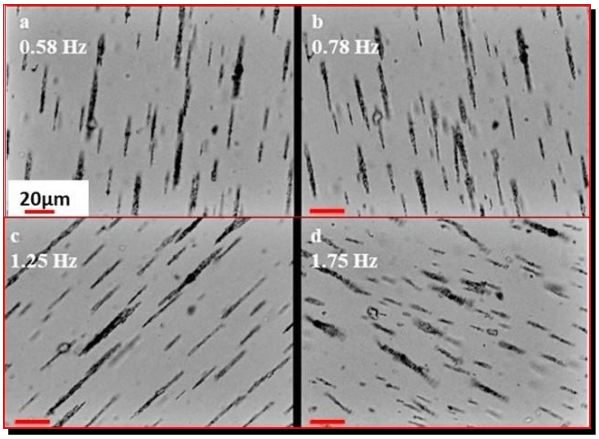

Fig. 3 – Nanoparticle chains in magnetic colloid with rotating magnetic field. (a-d) shows frequencies of 0.58, 0.78, 1.25 and 1.75 Hz respectively. Scale bar shows 20 μm

where H_0 is the applied magnetic field, χ is the particle susceptibility, μ_0 is permeability of vacuum, and volume of the particle $V = \pi d3/6$, where d is particle diameter. Two nearby particles with their dipole moments aligned, will have an interaction energy expressed by [25]:

$$U_{mag}(r,\alpha) = \frac{\mu^2}{4\pi\mu_0}\frac{\left(1-3\cos^2\alpha\right)}{r^3}, \quad (2)$$

where r is distance between particle centers and α is the angle between the particle centers and the applied field. The strength of the inter-particle interaction can be characterized by the magnetic coupling parameter given by the equation:

$$\Gamma = \frac{\mu_0 m_s^2}{2\pi d^3 k_B T}. \quad (3)$$

Based on the value of Γ which is 5, it can be clearly seen that the magnetic forces are strong enough to overcome the thermal agitation. This leaves us with only one competitive force i.e., the viscous force, which comes into effect during rotation. The rotational motion of a chain is governed by the balance between the applied magnetic torque and the viscous torque generated by the motion of the chain through the carrier medium. The magnetic torque generated on the chain is given by [25]:

$$\Gamma_m = \vec{\mu} X \vec{H}, \quad (4)$$

which induces rotational motion in the chains. Since there is a competition between the magnetic torque and the viscous forces, the ratio of viscous to magnetic forces on the chain can be a useful quantity which is known as the Mason number [25]:

$$M_n = \frac{32\eta\omega}{\mu_0\chi^2 H^2}. \quad (5)$$

Here η is viscosity and ω is frequency of rotation. As the magnitude of viscous forces increases, the value of M_n increases. With increasing frequency of rotation of the chains, the viscous forces start dominating. This results in the changing shape of the chains; the chains were seen to bend in the shape of the letter "*S*". In Fig. 3 and Fig. 4 it can be seen that the magnetic fluid chains bend with increasing frequency and at a frequency greater than 2 Hz, the chains break into smaller chains, or the chains ruptured into smaller fragments of chains.

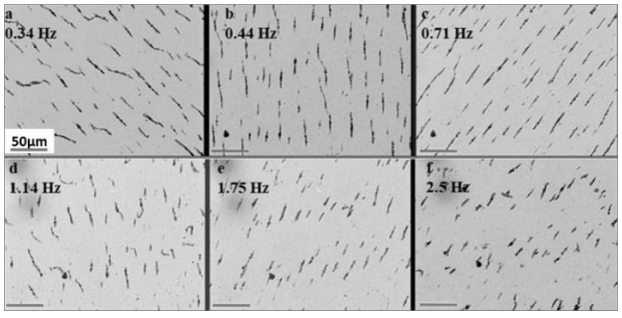

Fig. 4 – Nanoparticle chains in magnetic colloid with rotating magnetic field. (a-f) shows frequencies of 0.34, 0.44, 0.71, 1.14, 1.75, 2.5 Hz respectively. Scale bar shows 50 μm

To investigate the effect of micron sized magnetic particles on chain formation and its rotational dynamics, flake shaped Fe_3O_4 particles, having an average size of 30 μm, were suspended in the magnetic fluid medium. Fig. 5 shows the chain formation of two different size range magnetic particles in same fluid system. At frequency lower than 0.1 Hz, the head to tail attraction among neighboring chains resulted in longer chain formation. With increasing frequency, bending in the chains was observed and at frequency greater than 4 Hz very minute chains rotating at high speeds were observed which indicates rupture of chains.

Due to two different size range, this can be considered as a bi-dispersed system. The magnetic fluid surrounds the large particles and so considering it as a continuous medium (both hydrodynamically as well as magnetically), the magnetic permeability of micron-sized particles dispersed in ferrofluid can be estimated by the Maxwell-Garnett theory. The governing equation is [17]

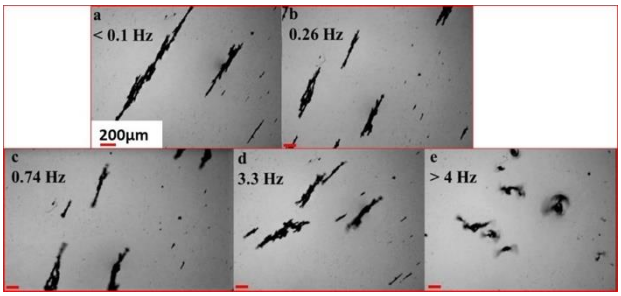

Fig. 5 – Chains of micron size magnetic particles dispersed in magnetic colloid. (a-e) show magnetic field rotating with increasing frequencies. Scale bar shows 200 μm

$$\mu = \bar{\mu}_{rf}\frac{1+2\Phi\beta}{1-\Phi\beta}, \quad (6)$$

where $\beta = \frac{\mu_{rp}-\mu_{rf}}{\mu_{rp}+2\mu_{rf}}$, μ is the relative permeability of bidispersed fluid, μ_{rf} is the relative permeability of magnetic fluid, μ_{rp} is relative permeabilityof micron-size magnetite particles dispersed in magnetic fluid, and β is the magnetic contrast factor. In this situation, the chain formation happens in a slightly different way. The nanoparticles tend to fit themselves in the gaps and microcavities inside the large chains or at the ends of the chains. During rotation, these chains also tend to bend in "*S*" shape but at a lower frequency compared to chains of nanoparticles alone (in a pure ferrofluid). The equation for magnetic force (F_d) on a dipole is given by [17]:

$$F_d = m(\nabla H), \quad (7)$$

where m is magnetic dipole moment. The general expression of particle motion under the influence of a rotating magnetic field is [17]:

$$\gamma' \frac{dx}{dt} = F_d + F_r + F_B, \quad (8)$$

where x is the position of particle, F_d is the dipolar magnetic force, F_r is the repulsive force, F_B is the

Brownian force, and $\gamma' = 6\pi\eta d$. Consequently, under rotating magnetic field, the large and small magnetic particle respond differently. The fragment of larger particle chains will orient in the direction of applied field more quickly compared to the smaller particles. In addition, due to Brownian movement of nanoparticles the probability of breakage of larger particle chains increases, and subsequently nanoparticles lag behind the rotation of larger particle chains. Due to lagging, the bending and increased flexibility of the chains are observed. Fig. 6 shows the microscopic image of bending of a single chain in bi-dispersed fluid. Nanoparticles are seen to be the connecting bridge between two large particles, forming a chain. Increasing frequency increases the lagging of nanoparticles inside this chain resulting in more twisting of the chain.

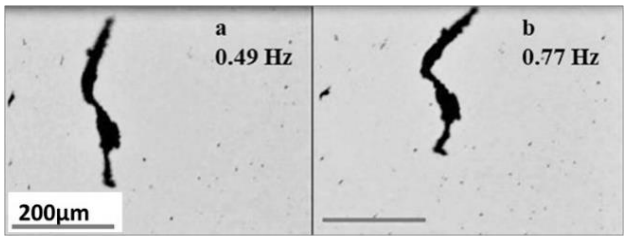

Fig. 6 – a-b show the increased twist in the chain with increased frequency. This later leads to the breakage of the chain into two parts. Scale bar indicates 200 µm

In the case of pure magnetic fluid, the chains had only the viscous forces in competition with the rotational magnetic forces whereas in bi-disperse fluid the lagging in magnetic response of nanoparticles during rotation was an additional factor along with the viscous forces for the bending of chains. Comparing the critical frequency for rupture of the chains, in the case of nanoparticles alone, the chains break at a frequency near 2 Hz while in the case of bi-disperse system, the rupture occurs at double frequency (4 Hz). Figure 7 and Figure 8 show the length of the rotating chains measured from the snapshots of microscopic images versus frequency of magnetic field. It is clearly seen that there is a sudden drop in the chain length in both cases which indicates the breaking of the chains into smaller fragments. This means that the inclusion of micrometer sized particles in ferrofluid increases the critical frequency for breaking of the chains. Hence the bi-disperse fluid chains were more flexible compared to magnetic fluid chains. In biological or microfluidic applications where active control over the size of chains is required, larger particles can be mixed with nanoparticles to create a bi-dispersed fluid to achieve better control over the size of chains.

To study the influence of non-magnetic micron sized particles on the chain formation and dynamics, expancel plastic microspheres of an average diameter of 100 µm were mixed in magnetic fluid and magnetic field was applied. It is a common conception that non-magnetic particles of large size may not be affected by inverse magnetophoretic effect. In our experiment, these particles were seen to form linear chain structures aligned in the direction of magnetic field. Fig. 9 shows the formation of linear chain structures of expancel microspheres after the magnetic field is applied. However, upon rotation of magnetic field, these "non-magnetic" chains were not able to rotate, irrespective of frequency. Fig. 10 shows the rotation of magnetic field with red arrow.

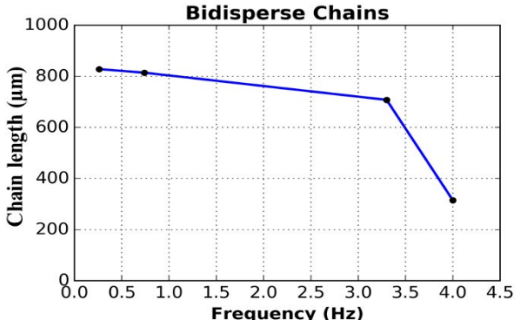

Fig. 7 – Chain length of nanoparticles vs frequency of magnetic field. The decrease in length indicates breaking of the chains

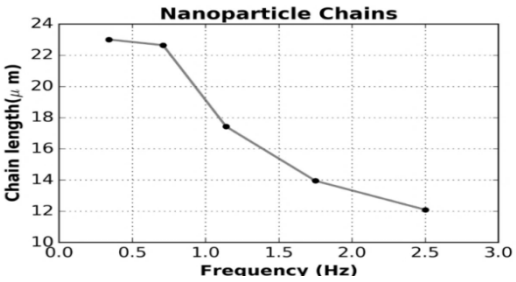

Fig. 8 – Chain length of bidisperse system vs frequency of magnetic field. The decrease in length indicates breaking of the chains

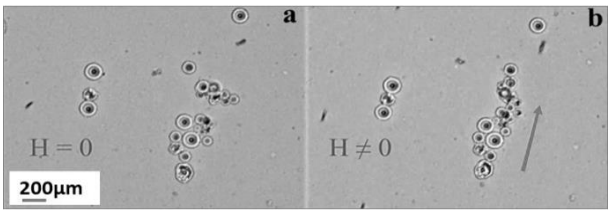

Fig. 9 – a) Expancel microspheres in the absence of external field. b) Formation of chains in the presence of magnetic field. Magnetic field intensity is 50 Gauss. Scale bar indicates 200 µm

Nearby magnetic fluid chains can be seen to rotate in the direction of magnetic field but the expancel spheres did not move. This can be explained by the adsorption of magnetic nanoparticles on the surface of these plastic spheres [26]. On application of magnetic field, these adsorbed particles gain their moments aligned in the direction of field. These surface adsorbed nanoparticles play the role of a connecting bridge between two spheres and due to attractive force of neighboring adsorbed particles, the chain formation of the spheres was possible.

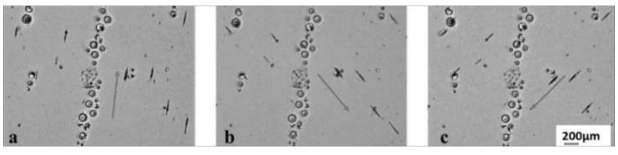

Fig. 10 – (a-c) shows the rotating magnetic field. Here the magnetic colloid chains are rotating along with the field but the expancel microsphere chains are not rotating

However, since there is no magnetic moment in the plastic spheres, the total magnetic moment of the chain was not sufficient for the magnetic force to generate a significant magnetic torque. Such non-magnetic particles included in a magnetic medium can serve as a controllable separator or valve between two regions of a single channel. Such separations can be controlled using magnetic field but can also stay unaffected by rotational magnetic field. If the volume fraction of magnetic fluid is increased, the number of particles will increase and hence number of chain formation will be increased. Similar results are expected if volume fraction of flake shaped particles and expancel microspheres is increased. Also, if the intensity of magnetic field is increased, chain formation may occur faster. To check these predictions in all the above experiments, extensive study of effect of the variation in volume fraction of magnetic fluid, flake shaped particles and expancel microspheres along with intensity of magnetic field will be done in future work.

4. CONCLUSIONS

Chain structure formation in magnetic fluid was studied under the rotational magnetic field. With higher frequency of rotation, bending and breaking of chains was observed due to increased viscous forces. Adding large magnetic particles resulted in more flexible chains due to lagging in nanoparticles' response to magnetic field rotation compared to large particles. Critical frequency for breaking of bidisperse chains was found to be greater than that for nanoparticle chains. Control of chain length can be achieved by adding larger particles which can help in microfluidics and biological applications. Addition of non-magnetic particles resulted in the formation of "non-magnetic" chains which was due to adsorption of nanoparticles on the surface of the plastic spheres. These chains remained unaffected by rotation of magnetic field due to insufficient magnetic moment of this chain. Such non-magnetic chains may serve as active separators or valves in a single microfluidic channel which can be controlled using magnetic field and yet remain unaffected by rotational variations in magnetic field.

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Магнітні наночастинки як регулятори ланцюгових структур в обертовому магнітному полі

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Спостерігалося утворення ланцюга в магнітній рідині під впливом обертового магнітного поля. Вплив на гнучкість ланцюга та його розрив вивчався шляхом зміни частоти обертання (1-5 Гц) магнітного поля фіксованої величини (50 Гс). Частинки Fe_3O_4 мікрометрового розміру та немагнітні розширювальні сфери фіксованої концентрації пізніше окремо суспендували в магнітній рідині. Був вивчений їх вплив на динаміку обертання ланцюга. Установлено, що критична частота розриву ланцюга була вищою в присутності більших магнітних частинок порівняно з магнітною рідиною окремо. Немагнітні частинки утворювали ланцюгові структури в присутності статичного поля, але не реагували на обертання магнітного поля. Теорія утворення магнітного ланцюга була використана для вивчення та обговорення результатів шляхом порівняння магнітних сил і сил в'язкості. Дослідження може бути корисним для контролю довжини та гнучкості ланцюга в мікрогідродинаміці.

Ключові слова: Магнітна рідина, Наночастинки, Магнітне поле.