Hydrodynamics of chains in ferrofluid-based magnetorheological fluids under rotating magnetic field

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Ferrofluid-based magnetorheological (MR) fluid is prepared by dispersing micron-size magnetic spheres in a ferrofluid. We report here the mechanism of chain formation in ferrofluid based MR fluid, which is quite different from conventional MR fluid. Some of the nanomagnetic particles of ferrofluid filled inside the microcavities are formed due to association of large particles, and some of them are attached at the end of large particles. Under rotating magnetic field, fragmentation of a single chain into three parts is observed. Two of them are chains of micron-size magnetic particles which are suspended in a ferrofluid, and the third one is the chain of nanomagnetic particles of ferrofluid, which may be the connecting bridge between the two chains of larger magnetic particles. The rupture of a single chain provides evidence for the presence of nanomagnetic particles within the magnetic field-induced chainlike structure in this bidispersed MR fluid.

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Conventional magnetorheological fluids (MR fluids) are prepared by suspending micron-size magnetically soft particles in a nonmagnetic liquid carrier. These fluids are complex and exhibit a remarkable change in their rheological properties under application of an external magnetic field [1–4]. The important characteristics of a MR fluid are its yield stress, viscosity, and settling rate. These properties can be tuned by applying external magnetic field for a desired application. MR fluids have been used in smart actuation systems, such as dampers, clutches, and isolators [5]. Recently, Mehta *et al.* [6–8] reported some unusual light scattering in ferrofluid based MR suspension. Some problems, such as particle aggregation and settling in MR fluids, restrict them for certain applications. To solve these problems, different procedures are adopted: (a) addition of thixotropic agents, (b) surfactants (c), and use of viscoplastic media or water-in-oil emulsions as continuous phases. But sometimes, these processes hinder the MR effects. Recently, it was demonstrated that the use of magnetite ferrofluid as carrier is an effective way to reduce the sedimentation of the micron-size particles in MR fluid [9,10]. The settling rate of micron-size particles in such bidispersed fluids is reduced because the microcavities created between the large particles are filled by nanomagnetic particles [11]. Melle *et al.* [12,13] theoretically and experimentally studied the dynamics of chain in conventional aqueous MR fluids under the application of rotating magnetic field using video microscopy and dichroism techniques. Breaking of chains in two fragments under rotating magnetic field (with rotating frequency 0.01 Hz), nonlinear chain shape, and possibility of brittle or ductile chain fracture were also studied for conventional aqueous MR fluids [12,13]. In this work, we report the (a) mechanism of magnetic field–induced chain formation in ferrofluid based MR fluid, which is quite different from the conventional MR fluid. In this ferrofluid-based MR fluid, 3-μm-sized magnetite particles are dispersed in kerosene-based magnetite ferrofluid. Using video microscopy experiment, it is observed that nanoparticles of ferrofluid are filled inside the microcavities formed between the aggregated large particles. This novel mechanism prevents the phase separation by reducing the field-induced aggregation of large magnetic particles which forms nonreversible structures and thus giving more stability to the chainlike structures. (b) Under rotating magnetic field, rupture of a single chain into two parts occurs at 6 times larger frequency than that observed for conventional MR fluid [12,13]. (c) Under rotating magnetic field, the breakup of a single chain into three fragments, i.e., two chains of micron-sized particles and a chain of nanomagnetic particles. The latter seems to act like a bridge between the two larger chains. This rupture provides evidence for the presence of nanomagnetic particles within magnetically induced chainlike structures in ferrofluid-based MR fluid and its importance in the stability of MR fluid.

Nanomagnetic particles of Fe_3O_4 were prepared by classical coprecipitation technique [14]. The stoichiometric mixture of solution containing ferric (Fe^{3+}) chloride and ferrous (Fe^{2+}) sulfate was introduced in alkaline solution. The resulting mixture was continuously stirred for 20 min at 10.5 pH to allow nanocrystallites to grow in size. Nanocrystallites were magnetically decanted and washed with distilled water several times to remove water soluble impurities. To obtain stable ferrofluid, these nanocrystallites were coated with oleic acid and dispersed in kerosene. The fluid was centrifuged at 12 000 rpm for 20 min to remove aggregates if any. From the magnetization measurements of the ferrofluid, average particle size (10.4 nm) and saturation magnetization of the fluid (200 Gauss) were determined. For the preparation of magnetorheological fluid (MRF), commercially available magnetite powder was used. Using fractional sedimentation, suspension of 3 μm size particles was obtained. Ferrofluid and magnetorheological fluid were diluted with kerosene so as to keep the number density of magnetic particles $\approx 10^{15}$ and 10^8 m^{-3}, respectively. Subsequently, both the samples were mixed and homogenized by ultrasonification. The visualization of chain dynamics under rotating magnetic field is observed using Magnus MLX microscope. The magnifica-

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tion used is 100x charge coupled device (CCD); camera used is Samsung (BW-360CD) attached with a personal computer. The sample is placed at the center of the two orthogonal pairs of Helmholtz coils which generate homogeneous rotating magnetic field up to 100 Oe in the plane of image.

In this bidispersed fluid, due to the dipole-dipole interactions, the individual dipoles are arranged in head to toe and tend to form stringlike structure in the direction of the force field. The dipole moment of a single particle in an applied magnetic field is given by $\mu = V\chi \mathbf{H_0}$, where $\mathbf{H_0}$ is the applied magnetic field, χ is the particle susceptibility, and volume of the particle $V = \pi d^3/6$, where d is the diameter of the particle. In our case, considering ferrofluid as a hydrodynamically and magnetically continuous medium [15], the permeability of micron-size magnetite spheres dispersed in kerosene-based magnetite ferrofluid can be calculated using the Maxwell-Garnett theory [16]

$$\mu = \mu_{rf}\frac{1+2\Phi\beta}{1-\Phi\beta}; \quad \beta = \frac{\mu_{rp}-\mu_{rf}}{\mu_{rp}+2\mu_{rf}}, \tag{1}$$

where μ is the relative permeability of bidispersed fluid, μ_{rf} is the relative permeability of ferrofluid, μ_{rp} is relative permeability of micron-size magnetite particles dispersed in ferrofluid, and β is magnetic contrast factor. Under the application of magnetic field, the induced dipoles interact with one another to form particulate aggregates. The formation of aggregates is opposed by Brownian dispersion and as such the potential for field-induced aggregation versus Brownian dispersion can be expressed in terms of a governing dimensionless parameter, known as coupling constant,

$$\lambda = \frac{\pi(\mu_0\chi H)^2 d^3}{18k_B T}, \tag{2}$$

where μ_0 and H are free space permeability and applied magnetic field, respectively. T and k_B are absolute temperature and Boltzmann constant. For $\lambda \gg 1$, aggregation is highly favored and $\lambda \ll 1$ dispersion is favored. The case of small λ is used as a design parameter for the ferrofluid, where larger value of λ commonly results in MR fluids [17]. For the sample used in this experiment, $\lambda = 200$ for micron-size magnetite spheres dispersed in a ferrofluid. Due to the presence of micron-size magnetic spheres in a ferrofluid, the aggregation parameters calculated for ferrofluid is

$$\lambda = \frac{\mu_0 M_s H \pi d^3}{6k_B T}, \tag{3}$$

where $\mu_0 M_s$ is saturation magnetization of the particles. For ferrofluid used in this experiment, $\lambda = 2.5$. The MR fluid microstructure due to shearing comes via the interplay of hydrodynamic and magnetic forces. The ratio of these interactions within an MR fluid forms a second dimensionless parameter known as Mason number,

$$M_n = \frac{9\sigma}{2(\mu_0\chi H)^2}, \tag{4}$$

where σ is the applied shear stress. As the M_n increases, the hydrodynamic viscous force dominates the magnetic dipolar force which restricts the field-induced linear aggregation of magnetic particles [18,19].

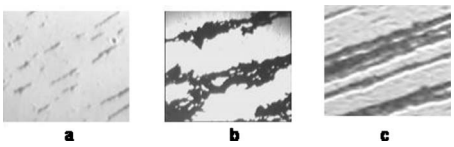

FIG. 1. Magnetically induced chainlike structure in magnetic colloids. (a) Ferrofluid; (b) conventional MR suspension; (c) bidispersed MR fluid, i.e., micron-size magnetic particles suspended in ferrofluid. In (c), the microcavities (pores) observed in conventional MR fluid are filled with nanomagnetic particles of ferrofluid.

Figure 1 shows the chain formation in three different magnetic colloids (i.e., ferrofluid, conventional MR fluid, and mixture of MR fluid and ferrofluid) under the influence of external magnetic field. These micrographs are taken at a magnetification of 100x. It is observed that all three pictures show quite different types of chain formation. Figure 1(a) shows the formation of chain in a ferrofluid which contains nanomagnetic particles (~10 nm) of magnetite dispersed in kerosene. Figure 1(b) shows the chain formation in conventional MR fluid. It shows high networking of micron-size magnetic particles ~(3 μm) in which microcavities are observed. Figure 1(c) shows the chain formation in bidispersed MR fluid, i.e., mixed system of ferrofluid and conventional MR fluid. In this bidispersed system, it is observed that the open microcavities in Fig. 1(b) are filled by nanomagnetic particles of ferrofluid [see Fig. 1(c)] [11]. The coupling parameter λ is the key quantity that determines the equilibrium structure of a suspension of magnetic particles as a function of applied magnetic field. The coupling parameter λ for micron-size particle is very much larger (200) than that of nanomagnetic particles (2.5). This suggests that the dipolar interaction between the micron-size magnetic particles is much stronger than it is for nanomagnetic particles. Due to this reason, there is a possibility of large aggregation of micron-size magnetic particles under the influence of magnetic field which leads to phase separation. But when nanomagnetic particles are mixed with micron-size particles, the homogeneous distribution of small particles changes the effective magnetic permeability of the break ground for the large particles, which reduces the effective dipolar interaction between large particles. Hence, some of the nanomagnetic particles sit inside the structural cavities formed by large particles and some may be attached at the end of the large particles. Thus, nanomagnetic particles of ferrofluid prevent larger aggregations of micron-size magnetic particles leading to a phase separation of micron-size magnetic particles. This mechanism gives more stability of chainlike structure in ferrofluid-based MR fluid. Figure 2 shows dynamics of structure as a function of frequency of rotating magnetic field ($H = 20$ Oe). Each shot is recorded at an interval of 500 s. As the frequency of rotation of magnetic field increases, the Mason number M_n increases. Hence, hydrodynamic viscous force dominates the magnetic dipolar force and $l \propto \frac{1}{\sqrt{M_n}}$ suggests that the length of linear chain decreases [Figs. 2(a)–2(d)]. At $f = 6$ Hz and $M_n > 1.8$, more isotropic structures and isolated particles appear. In the case of con-

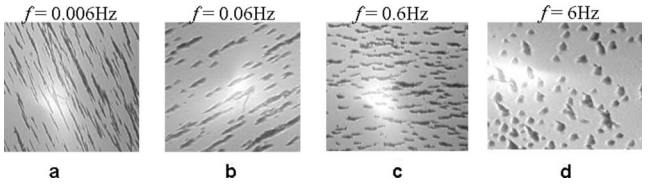

FIG. 2. Shows videomicroscopy (at 500 s) for bidispersed system composed of micron-size magnetic particles dispersed in ferrofluid, with increasing frequency of rotating magnetic field. As the frequency of rotation increases, (a) linear structure deforms slightly, further increasing the frequency of rotation; [(b) and (c)] it breaks in to smaller chains; (d) at $f=6$ Hz linear aggregation of particles is hindered and more isotropic structures appear.

ventional MR fluid, this behavior is observed for $M_n \geq 1$ [12,13]. Figure 3 shows dynamics of a single chain with increasing frequency under rotating magnetic field. Initially, when $f=0$ and under the application of external magnetic field, a head to tail arrangement forming linear chain of magnetic particles is observed [Fig. 3(a)]. As the frequency of rotating magnetic field increases, the hydrodynamic viscous force increases compare to magnetic dipolar force. Under this condition, two ends of the chain remains in the direction of the applied field due to free dipoles of large particles at the end but the central region of the chain of small particles lags behind due to more viscous force than the magnetic dipolar force. Following the competition between these two forces, it attains mirror S shape [Fig. 3(b)]. But when the hydrodynamic viscous force dominates the magnetic dipolar force, it breaks into two parts from the middle [Fig. 3(c)]. After the fragmentation, both the fragments remain aligned in the direction of the applied external magnetic field. Here in the case of ferrofluid-based MR fluid, the critical frequency at which the break up of a single chain occurs is 0.06 Hz, which is 6 times larger than that for the conventional MR fluids (i.e., 0.01 Hz) [12,13]. Further increasing the frequency of rotating magnetic field (i.e., 0.1 Hz), three fragments of a single chain is observed. Two of them are chains of large magnetic particles and the middle one is a small chain of nanomagnetic particles [Fig. 3(d)]. This observation suggests that nanomagnetic particles of ferrofluid play vital role in magnetic field-induced chainlike structure in ferrofluid-based MR fluid. The above-observed effects can be further explained as given below.

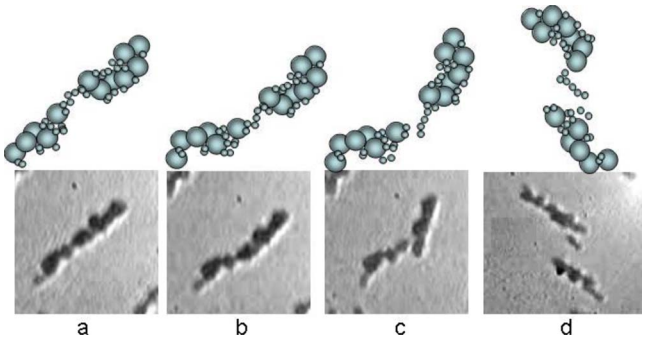

FIG. 3. (Color online) In the case of bidispersed fluid, three fragmentations of single chain are observed (schematic as well as microscopic pictures are shown). (a) Linear structure of magnetic particles under the effect of magnetic field at $f=0$ Hz; (b) at $f=0.006$ Hz, deformation of linear chainlike structure under rotating magnetic field; (c) at $f=0.06$ Hz breaking of chains in two parts; (d) further increasing the frequency of rotating magnetic field to 0.1 Hz, breaking of chain into three parts, i.e., two chains of large magnetic particles and in-between chain of aggregated nanomagnetic particles of ferrofluid. *Schematic:* (a) shows association and location of nanomagnetic particles with the two chains of large magnetic particles under the effect of external magnetic field; (b) deformation of linear structure under the application of rotating magnetic field (mirror S shape) at 0.006 Hz; (c) breaking of nanoparticle contact from one of the large particle chain at $f=0.06$ Hz; (d) further increasing the frequency of rotating magnetic field to 0.1 Hz, breaking of nanoparticle contact from the other chain of large particles giving evidence of nanoparticle bridge between the two chains of large magnetic particles.

It is known that magnetically induced chain formation in MR fluids is one of the most important properties which modulate its rheological and optical properties that determine its different potential applications. In this experiment, the ferrofluid-based MR fluid is a bidispersed system of hard spheres with same dipole moment but with different diameters. The mechanism of magnetically induced chain formation in bidispersed magnetic colloids is theoretically studied by Wang and Holm [20] and Ivanov and Kantorovich [21]. The dipole moments of particles are proportional to its volume; hence at low-field strength, larger particles can be oriented more easily toward the applied field direction. Considering small fraction of large particles and large fraction of small particles, the dipole-dipole interaction energy between larger particles will be greater than the thermal energy at room temperature. Due to this reason, they aggregate into zero fields and field-induced different structures. The most probable structural character in these types of bidispersed systems is head to toe chainlike aggregates formed by large particles and some small particles might be attached to the ends of large particles and also within the microcavities of the aggregated structures. The dipole-dipole interaction potential between particles i and j is given by

$$U_{ij}^{dip} = \frac{1}{4\pi\mu_0}\left[\frac{\boldsymbol{m}_i \cdot \boldsymbol{m}_j}{r_{ij}^3} - \frac{3(\boldsymbol{m}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{m}_j \cdot \boldsymbol{r}_{ij})}{r_{ij}^5}\right], \qquad (5)$$

where r_{ij} is the displacement vector of the two particles and μ_0 is the vacuum permeability; $\boldsymbol{m}$ is the respective dipole moments. Energetically, there are two possibilities that small particle attach with the chain of large particles. One moving from transverse direction perpendicular to chain and trapped at triangular position between two large particles and other being attached at the free end of chain [20,21]. With these possibilities, nanomagnetic particles of ferrofluid can fill microcavities within the structure formed by large particles and attach at the free end of the chain formed by large particles. Energy considerations suggest that the probability of small particles attaching at the end of the chain is more [20]. Thus, two short chains of large particles with small particles at their ends approach each other; combine to form a longer chain. Hence, small particles at lower end of one chain and at upper end of the other behave as a connecting bridge be-

tween two chains of large particles. Considering a magnetic field rotating in x-y plane $\boldsymbol{H_0}=\boldsymbol{H_0}$ $(e_x \cos \omega t + e_y \sin \omega t)$, then the interaction energy corresponding to the two dipoles $\boldsymbol{m_\alpha}=\boldsymbol{m_\beta}=m(e_x \cos \omega t + e_y \sin \omega t)$ rotating in phase with the field, whose average on a period gives $W=m^2/2r^3$ $(3\cos^2\theta-1)$, where θ is the angle from z axis. Here, each dipole feels the applied field plus this dipole field. The general expression for the magnetic force on the dipole is $\mathbf{F_d} \propto \mathbf{m}\cdot(\nabla \mathbf{H})$, where $\mathbf{m}$ is the dipole moment. Thus, under the rotating magnetic field, the response of larger particle toward the magnetic field will be more than the smaller particles in the chain. Hence, the chains formed by larger particle will try to align in the direction of applied rotating field more rapidly than that of the chain formed by the smaller particles; also Brownian movement of small particles enhances the breakup probability of larger particle chains and subsequently small particles lags behind the rotation of large particle chains. As observed in Figs. 3(a)–3(d), when frequency of rotating magnetic field increases, the linear-chain structure deforms and takes up mirror S shape due to the competition between hydrodynamic viscous force and dipolar magnetic force. In the formation of mirror S shape, the arms of the chain (larger particles) are moving faster to follow the field direction and the response of smaller particles in the middle is less than the rotating magnetic field. In this case, the generalized equation of motion of particles under rotating magnetic field can be given as $\gamma\ (dr/dt)=\mathbf{F}_d+\mathbf{F}_r+\mathbf{F}_B$, where r is the position of particle, $\mathbf{F}_d$ is the dipolar force, $\mathbf{F}_r$ is the repulsive force, $\mathbf{F}_B$ is the Brownian force, and $\gamma=6\pi\eta a$, where a is the radius of the particle and η is the viscosity of the fluid. In this bidispersed system, as the probability of attaching small particle at the end of large particle is maximum [20], two short chains with small particles at their ends approach each other and combine into a longer chain. The binding energy between small and large particle is also not strong enough. Hence, under rotating magnetic field, when hydrodynamic viscous force and subsequently the Brownian force overcomes the dipolar magnetic force, the small particles attached with one of the chains of large particles becomes free and break the chain into two parts [Fig. 3(c)]. Further increasing the frequency of rotation increases the hydrodynamic viscous force on the particles, such that the nanomagnetic particles attached with the other chain of large particles loses the contact and becomes free. Thus, a single chain composed of nanomagnetic particles in the middle and chains of large magnetic particles at the ends break into three components: two chains of large magnetic particles and one chain of nanomagnetic particles. These results clearly indicate that small chain of nanomagnetic particles acts like a bridge between the two chains of large magnetic particles.

It is observed that the mechanism of magnetically induced chain formation in ferrofluid-based MR fluid is quite different from that of conventional MR fluid. Here, the nanomagnetic particles of ferrofluid hinder the magnetically induced large aggregation of micron-size magnetic particles by changing the effective permeability of the large particles with respect to background of ferrofluid and due to attachment of small particles inside the cavities formed by large particles and at the end of large particles. The structure formed by the combination of small and large magnetic particles gives more stability to MR fluids. Due to the probability of small particles attaching at the end of the chain formed by large particles, under the application of magnetic field, when two chains combine nanomagnetic particles of ferrofluid behaves like a bridge between the chains of large particles. The rupture of a single chain into three parts provides evidence of the presence and active participation of nanomagnetic particles within the structure formation by large particles.

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