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MR fluid structure in quasi-2D

R. Haghgooie and P. S. Doyle

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MR fluid structure in quasi-2D

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Abstract – We study the effects of quasi-two-dimensional (quasi-2D) confinement on the self-assembly of super paramagnetic colloids found in magnetorheological (MR) fluids using the Brownian dynamics simulation technique. A uniform external magnetic field is directed normal to a thin-slit in which dilute MR fluid is confined. The thickness of the confining slit ranges from a single colloid diameter to several colloid diameters. The steady-state structure that forms under such extreme confinement is shown to depend heavily upon the thickness of the slit. As the slit-thickness is increased from one colloid diameter (2D confinement) the structure of the dilute MR fluid changes non-monotonically. We introduce a ground-state model to predict the structure as a function of the slit-thickness and the volume fraction of the fluid. The model is able to quantitatively predict the structures observed in our simulations.

Introduction. – Confinement of two-dimensional (2D) colloidal systems in the lateral directions can cause important changes in the properties of the system [1–3]. Likewise, the relaxation of strictly 2D colloidal systems to quasi-2D confinement can induce drastic changes in structure [4]. Of particular interest is the structure of self-assembled magnetorheological (MR) fluids confined in the thin-slit geometry [5,6]. This system is of interest from both a fundamental science standpoint as a model for the effects of confinement on self-assembly [5] as well as for practical applications such as microfluidic DNA separations [6]. Previous studies of the self-assembly of MR fluids in thin-slits have focused on slit-thicknesses ranging from ∼10 to 1000's of colloid diameters [5,7–9] or purely 2D systems where the slit-thickness is one colloid diameter [10–12]. The range of slit-thicknesses from one to ten colloid diameters is of great importance as many interesting phenomena occur during the self-assembly of MR fluids under such confinement but it has yet to be explored in the literature. Furthermore, the characteristic length-scales in microfluidic devices have continued to shrink down to this range of sizes making it of practical importance as well.

The structure that forms in thin-slits when an MR fluid is exposed to a uniform external magnetic field, normal to the slit, depends upon the volume fraction of the fluid and the strength of the external field. When the volume fraction is low, the colloids in the MR fluid self-assemble into columns spanning the height of the slit and separated by a characteristic distance (or pore size) [5]. At higher volume fractions, labyrinth (or striped) structures can form [13]. As of yet, the self-assembly of dilute MR fluids under extreme confinement (< 10 colloid diameters) has not been studied although it is highly relevant for microfluidic applications [6,14]. Some work has been done to study the self-assembly of concentrated MR fluids (> 0.2 volume fraction) under this extreme confinement but the structures that form at such high concentrations differ greatly from the ones presented here [13]. In this letter, we present the first study of self-assembled dilute MR fluids under extreme confinement (< 10 colloid diameters) in thin-slits. Using the Brownian dynamics simulation technique, we investigated the structure of the fluid under the application of a uniform external magnetic field normal to the thin-slit. We are interested in studying the phase space that is practical for the microfluidic DNA separation devices mentioned previously, namely volume fractions < 0.1 and external fields that are sufficiently large to cause structure formation but small enough that they can be experimentally realized.

Simulation details. – We used the Brownian dynamics (BD) simulation technique to model the self-assembly of the MR fluid in thin-slits [15–17]. In this

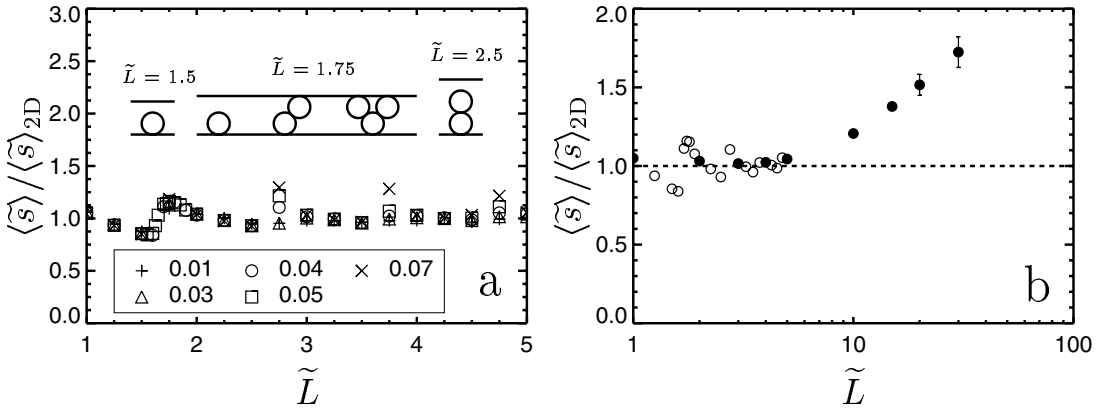

Fig. 1: Average dimensionless spacing normalized by the 2D spacing as a function of dimensionless slit-thickness for (a) five different volume fractions and (b) $\phi = 0.04$, both at a dimensionless field strength of $\lambda = 50$. The types of clusters observed in our simulations are shown for three dimensionless slit-thicknesses (1.5, 1.75, and 2.5) as insets in (a). The horizontal dashed line in (b) is for $\langle\widetilde{s}\rangle = \langle\widetilde{s}\rangle_{2D}$. The closed circles in (b) represent integer values of $\widetilde{L}$.

system, lengths were made dimensionless with the colloid diameter d and times were made dimensionless with the diffusive time scale $[\widetilde{t} = t(k_B T)/(\zeta d^2)]$, where $(\zeta d^2)/(k_B T)$ is the time for a colloid to freely diffuse a distance equivalent to its diameter d. The parameter ζ is the Stokes drag coefficient on a single colloid, assumed to be constant in this work. Additionally, hydrodynamic interactions between the colloids were neglected for simplicity. The deterministic forces in this system were due solely to the magnetic interactions between the colloids. The dimensionless interaction energy between two MR colloids is given by

$$\widetilde{U}_{ij}\left(\widetilde{r}_{ij}, \theta_{ij}\right) = \frac{1}{2}\lambda\left(\frac{1 - 3\cos^2\theta_{ij}}{\widetilde{r}_{ij}^3}\right), \tag{1}$$

where $\widetilde{r}_{ij}$ is the distance between colloids i and j, θ_{ij} is the angle made by the vector connecting the centers of the two colloids and the external field vector, and λ is the dimensionless external field strength defined as the ratio of the maximum magnitude magnetic energy between colloids to the thermal energy in the system [5]

$$\lambda \equiv \frac{-U(d,0)}{k_B T} = \frac{\pi \mu_0 d^3 \chi^2 H_0^2}{72 k_B T}. \tag{2}$$

In eq. (2), μ_0 is the magnetic permeability of free space, χ is the effective magnetic susceptibility of one colloid, and H_0 is the magnitude of the uniform external magnetic field.

The equation of motion was integrated forward in time using a simple Euler integration scheme with a dimensionless time-step of 10^{-4}. At the end of a time-step, hard sphere overlaps were treated by displacing overlapped colloids along the line connecting their centers until they are just contacting [18]. This procedure was performed for all overlaps, between two colloids and between colloids and hard walls [16,17], and was iterated until all overlaps in the system were removed. The simulations were started from a random starting configuration and the external magnetic field strength was ramped continuously from $\lambda = 0$ to $\lambda = 50$ over a dimensionless time of 100 after which it was held constant at $\lambda = 50$. Ramping the external magnetic field over a longer time did not change the final properties measured in the simulations. All of the simulations were determined to be converged in system-size, time-step, and ramp-time for the external magnetic field.

The boundary conditions of the simulations in this work were periodic in the x- and y-directions and hard-walls in the z-direction. The uniform external magnetic field was directed in the z-direction (normal to the thin-slit) causing the MR colloids to self-assemble into column structures spanning the height of the thin-slit. Simulations were performed for the self-assembly of five different volume fractions of MR fluid ($\phi = 0.01$, 0.03, 0.04, 0.05, and 0.07) in thin-slits ranging in dimensionless thickness from $\widetilde{L} = 1$ to 30.

Quasi-2D thin-slits. – For dilute MR fluids confined in thin-slits, the separation between clusters $\langle\widetilde{s}\rangle$ has been an important way to characterize the structure of the sysem [5,7,19]. In purely 2D colloidal systems, the clusters are composed of single MR colloids separated by a characteristic distance $\langle\widetilde{s}\rangle_{2D} = \sqrt{\pi/3\phi\sqrt{3}}$ that depends upon the volume fraction in the system [16]. As the 2D confinement is relaxed to quasi-2D, the spacing between the clusters changes as illustrated in fig. 1, where we show the normalized dimensionless spacing between clusters as a function of slit-thickness for five different volume fractions. The spacing between the clusters clearly changes as the slit-thickness increases but the trends are non-monotonic and instead the spacing is seen to oscillate around the 2D value (fig. 1a) before departing completely around $\widetilde{L} = 10$ (fig. 1b). The departure from quasi-2D behavior

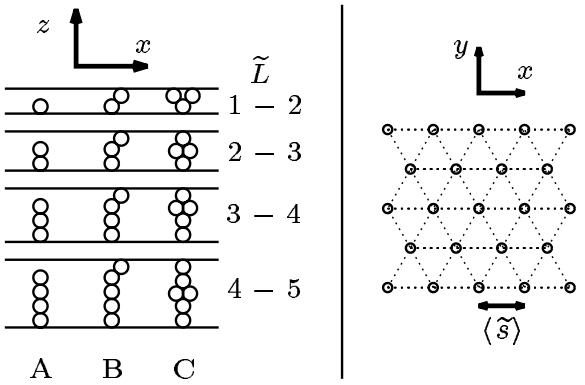

Fig. 2: Left: a schematic of the possible types of clusters for each range of dimensionless slit-thicknesses considered. Right: a schematic of the hexagonal lattice of clusters with lattice spacing $\langle\widetilde{s}\rangle$. A lattice site can be occupied by any of the three cluster types A, B, or C.

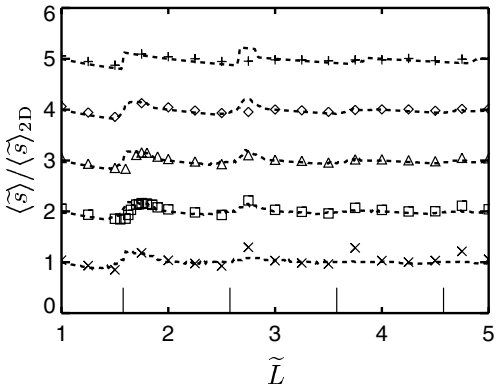

Fig. 3: Normalized dimensionless spacing as a function of slit-thickness for $\phi = 0.01$, 0.03, 0.04, 0.05, and 0.07 (from top to bottom) for $\lambda = 50$. The curves are shifted by 1 with respect to one another for ease of viewing. The dashed lines are the predictions from the ground-state model for each ϕ. The long vertical ticks along the $\widetilde{L}$ axis denote the points $n + \sqrt{1/3}$ where n is an integer.

in fig. 1b will be discussed elsewhere [20]. The structure of concentrated MR fluids ($\phi = 0.2$) has been shown to oscillate between disorder and labyrinth structures in extremely thin-slits [13] but the oscillations in spacing of confined dilute MR fluid structures have not been previously observed.

Schematics of the dominant types of clusters that form in three different slit-thicknesses are shown in fig. 1a as well. Based on observations of the cluster types in these systems, we determined that the oscillations in spacing with increasing $\widetilde{L}$ are due to geometric effects in the case of declining spacing or energetically favorable rearrangement of the cluster types in the case of increasing spacing. In 2D ($\widetilde{L} = 1$) the colloids experience purely repulsive interactions and the spacing is determined simply by geometry [16,17]. As the slit-thickness increases, the colloids still experience repulsive interactions for $\widetilde{L} < 1 + \sqrt{1/3}$ and therefore the clusters remain just single colloids. In order to maintain a constant volume fraction of MR colloids the clusters must be closer to one another, hence the decrease in spacing. Once the slit-thickness becomes large enough, $\widetilde{L} \sim 1.75$, the MR colloids can have attractive interactions and begin to form clusters larger than a single colloid. The spacing is proportional to the average cluster size and therefore it increases sharply as more large clusters are formed. This process is repeated between each integer value of $\widetilde{L}$ and the oscillations in fig. 1 therefore occur roughly at $\widetilde{L} = n + \sqrt{1/3}$ where n is an integer.

Using simple geometric arguments, the spacing between clusters is related to the average cluster size ($\langle c\rangle = N/N_{\rm clust}$) as $\langle\widetilde{s}\rangle \approx \sqrt{(\pi\langle c\rangle)/(3\phi\widetilde{L}\sqrt{3})}$, where N is the number of colloids and $N_{\rm clust}$ is the number of clusters in the system. This relation is useful if we are able to predict the types of clusters that form as a function of slit-thickness. Therefore, we developed an energy model to predict the ground-state structure of the system applicable to the case of extremely thin-slits. Our model consists of three possible types of clusters arranged on a hexagonal lattice with a spacing defined by the average cluster size as shown in fig. 2. We chose three types of clusters in order to limit the degrees of freedom in our model such that we were able to easily find a solution. The three types of clusters (A, B, and C) vary depending upon the slit-thickness. For instance, when $1 \leqslant \widetilde{L} < 2$ the clusters A, B, and C are a "singlet", "doublet", and "triplet" arranged as shown in fig. 2.

Using the model as outlined, we varied the concentrations of clusters ($\phi_{\rm A}$, $\phi_{\rm B}$, $\phi_{\rm C}$) in order to minimize the total energy per colloid. The cluster concentration is defined as $\phi_i \equiv N_i/N_{\rm clust}$, where N_i is the total number of clusters of type i and $N_{\rm clust}$ is the total number of clusters. The total energy per colloid is the sum of the intra- and inter-cluster energies per colloid, defined as $(\widetilde{U}_{\rm tot}/N) = (\widetilde{U}^{\rm intra}_{\rm tot}/N) + (\widetilde{U}^{\rm inter}_{\rm tot}/N)$. The total intra-cluster energy per colloid is defined as

$$\frac{\widetilde{U}^{\rm intra}_{\rm tot}}{N} = \frac{N_{\rm A}\widetilde{U}^{\rm intra}_{\rm A} + N_{\rm B}\widetilde{U}^{\rm intra}_{\rm B} + N_{\rm C}\widetilde{U}^{\rm intra}_{\rm C}}{N_{\rm A}n_{\rm A} + N_{\rm B}n_{\rm B} + N_{\rm C}n_{\rm C}}, \qquad (3)$$

where n_i is the number of MR colloids in a cluster of type i and $\widetilde{U}^{\rm intra}_i$ is calculated by summing all of the interaction energies between the colloids in a cluster of type i. The total inter-cluster energy is defined as

$$\frac{\widetilde{U}^{\rm inter}_{\rm tot}}{N} = \frac{1}{2}\frac{\sum_i^{\rm A,B,C}\sum_j^{\rm A,B,C}\phi_i\phi_j\widetilde{U}^{\rm inter}_{ij}}{\phi_{\rm A}n_{\rm A} + \phi_{\rm B}n_{\rm B} + \phi_{\rm C}n_{\rm C}} \qquad (4)$$

and the energy $\widetilde{U}^{\rm inter}_{ij}$ is defined as

$$\widetilde{U}^{\rm inter}_{ij} = \sum_{\rm lat}\left\langle\widetilde{U}^{\rm clust}_{ij}(\widetilde{r}_{\rm lat})\right\rangle, \qquad (5)$$

where the sum is over all the lattice sites and the term $\widetilde{U}^{\rm clust}_{ij}(\widetilde{r}_{\rm lat})$ denotes the energy between a cluster of

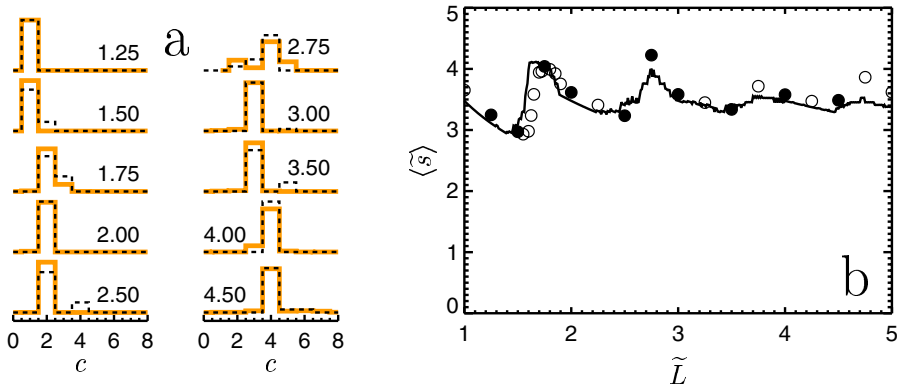

Fig. 4: (a) (Color online) Cluster size distributions for $\phi = 0.05$ in a variety of dimensionless slit-thicknesses. The orange solid line is the distribution observed in the BD simulations and the dashed black line is the prediction from the ground-state model. (b) The average spacing between clusters as a function of dimensionless slit-thickness for $\phi = 0.05$. The solid line is the prediction from the ground-state model and the symbols are the simulation results. The closed symbols denote the slit-thicknesses presented in (a).

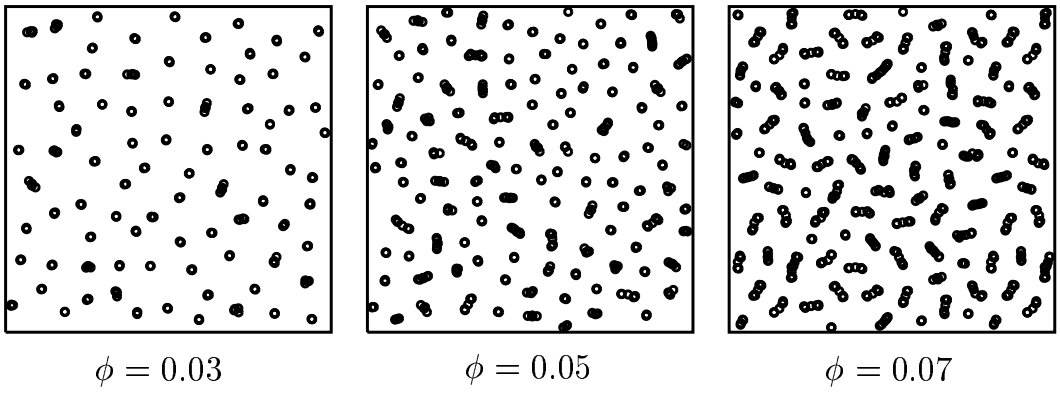

Fig. 5: Top-down views of the steady-state structure in our simulations for $\widetilde{L} = 3.75$ and $\lambda = 50$. The external magnetic field is directed out of the page.

type i and a cluster of type j separated by a distance $\widetilde{r}_{\text{lat}}$. The dimensionless distance $\widetilde{r}_{\text{lat}}$ is determined by both the characteristic spacing $\langle \widetilde{s} \rangle$ and the specific lattice site. The $\langle\rangle$ brackets in eq. (5) denote an angle-averaged energy meaning we allow the two clusters to rotate with respect to one another keeping their center-of-mass separation equal to $\widetilde{r}_{\text{lat}}$ and take their average interaction energy. We summed over a large enough lattice such that increasing the number of sites did not change the results. Additionally, we confirmed that the incorporation of the effects of mutual induction [21] between the colloids did not significantly affect the results of our model.

Once we found the distribution of cluster concentrations (ϕ_{A}, ϕ_{B}, ϕ_{C}) that minimized the energy per colloid for a given $\widetilde{L}$ and ϕ we calculated the average cluster size and therefore the average spacing between clusters. In fig. 3 we show the normalized average spacing between clusters as a function of dimensionless slit-thickness for all five volume fractions from both our simulations (symbols) and our ground-state model (dashed lines). The curves are shifted for ease of viewing. The predictions from our model match well with the simulation results for most slit-thicknesses. In particular, the model correctly predicted the magnitude and locations of the oscillations in the spacing as a function of the slit-thickness.

The cause of the oscillations (geometric effects and re-arrangement of the cluster types) was confirmed by both the model and the simulation results. In fig. 4 we show the predictions for the cluster distributions and spacing between clusters for a volume fraction of $\phi = 0.05$. In fig. 4b, the oscillations in spacing are quite obvious and the zero temperature model clearly predicts the spacings observed in our BD simulations. Additionally, in fig. 4a the cluster distributions predicted by the model are also found in the simulations. The oscillations are shown to be correlated with the changes in the cluster distributions. For instance as $\widetilde{L}$ increases from 2.5 to 3 the average cluster-size changes from 2 to 3 but at the point $\widetilde{L} = 2.75$ the average cluster-size is even larger (including clusters of size 5). As a result, the spacing between clusters oscillates

over this range of slit-thicknesses. From $\widetilde{L}=3$ to 3.5 the average cluster-size remains constant and therefore the spacing decreases as a result of the geometric constraint due to the constant volume fraction.

For slit-thicknesses of $\widetilde{L}=2.75$, 3.75, and 4.75 the data in fig. 1a do not collapse by normalizing with the 2D spacing. The increasing spacing as a function of the volume fraction in this case has to do with the approach to the labyrinth structure observed in other studies [13]. As the volume fraction is increased at these particular non-integer values of slit-thickness, $\langle c \rangle$ increases and the structure of the system begins to resemble the labyrinth structure. Ukai *et al.* observed labyrinth structures for $\widetilde{L}=3.8$ and $\phi=0.2$ and in fig. 5 we show the approach to the labyrinth structure for $\widetilde{L}=3.75$ in our simulations. As the volume fraction is increased in fig. 5, the clusters become much larger and more wall-like.

Conclusions. – In this letter, we have shown that the relaxation of the 2D confinement of dilute MR fluids to quasi-2D confinement results in non-monotonic behavior of both the cluster types in the system and the spacing between those clusters. We have presented a ground-state model for the structure of the system as a function of dimensionless slit-thickness and volume fraction of the MR fluid. The ground-state model is able to predict the types of clusters that form under quasi-2D confinement. The cause of the oscillations in the spacing between clusters in this system has been presented and confirmed by both our simulation results and the ground-state model. At certain non-integer slit-thicknesses, we have shown how the structure in this system approaches the previously observed labyrinth structure [13] as the volume fraction of the MR fluid is increased.

The reduction in the sizes of microfluidic devices has created a need for studying how such extreme confinement affects existing technologies. Dilute MR fluids have been used as structural components in these geometries but as of yet, there has not been a study of the effects of extreme confinement on the structures that self-assemble under the application of an external magnetic field. We have shown that even small changes in the confining geometry can have drastic effects on the pore size (cluster spacing) in thin-slits which could prove useful in designing the DNA separation devices mentioned previously [6]. Additionally, we expect that the results presented here will serve to illuminate the important properties of self-assembled MR fluids in quasi-2D confinement.

* * *

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