# Conformational Changes of Magnetic Dipolar Chains at a One-Dimensional Interface

## H. Z. Wen,\* L. E. Helseth, and T. M. Fischer

Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306-4390 Received: June 1, 2004; In Final Form: July 16, 2004

We visualize the conformational changes of paramagnetic particle chains at a one-dimensional interface. By tuning the strength of the external magnetic field, we changed the stiffness of the particle chains and their conformations at the interface. It is found that in the absence of an external magnetic field the particle chains easily undergo conformational changes, while in stronger fields they tend to keep their chain shape. In fields of intermediate strength, adsorption at the interface transforms the chains into stable pyramids.

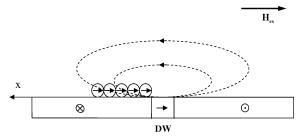
## 1. Introduction

Conformational changes of molecules have been extensively studied for many years.<sup>1,2</sup> However, the direct visualization of conformational changes is difficult. On the other hand, magnetorheological fluids are capable of forming dipolar chains of tunable stiffness in external fields which can be visualized directly using electron or light microscopes.<sup>3–13</sup> These chains may undergo conformational changes upon adsorption to magnetic domain walls (DWs), which is a very interesting phenomenon, although quite different from the case in nonmagnetic systems (e.g., biopolymers), where van der Waals forces and electrostatic forces are dominant for conformational changes.

In this work, we visualize the conformational changes of paramagnetic particle chains at a one-dimensional interface using a manipulation technique for colloidal particles that relies on DWs in magnetic garnet films, <sup>14</sup> which was recently demonstrated by our group. A microscope images the particles resting on the magnetic film. The particles deposited on the magnetic film form chains along the magnetic field and adhere at the DWs. When adsorbing at the DW, the particle chains undergo conformational changes, which arise from the competition of the dipole interaction between the beads and the attractive interaction of the bead with the DW. By tuning the external magnetic field, one can change the stiffness of the particle chains and, thus, the conformations of the chains at the DW.

## 2. Experimental Section

The DWs are formed in a bismuth-substituted ferrite garnet film with a thickness of 4  $\mu$ m and a magnetization of  $M_{\rm s}=10^5$  A/m by creating stress points near the edge of the film. <sup>15</sup>A plastic ring with a diameter of ~2 cm is placed on top of the garnet film, and beads immersed in pure water at a density of  $\rho \sim 10^7$  beads/mL were confined within this ring. The particles used here are paramagnetic beads manufactured by Dynal (Dynabeads M270) and coated with a carboxylic acid (COOH–) group, each with a radius of  $a=1.4~\mu$ m. The domain wall acts as a one-dimensional interface, where the beads adsorb (see Figure 1). An external magnetic field parallel to the magnetic film along the DW normal aligns the magnetic moments of the beads perpendicular to the wall. Sufficiently strong external fields enforce the minimization of the dipolar interaction between the beads and therefore cause the formation of bead



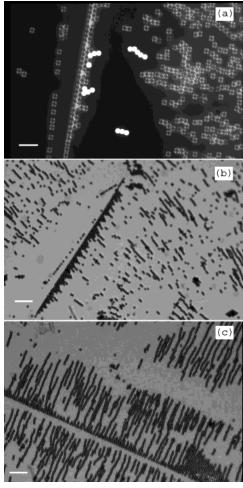
**Figure 1.** Schematic illustration showing the formation of a bead chain which is trapped by the DW. In the example shown here, the DW is a Néel wall.

chains perpendicular to the DW. When a bead chain reaches the interface, it may undergo a conformational change, which can be visualized with a polarization microscope (Leica DMPL). By tuning the strength of the field between 0 and 500 A/m, one changes the stiffness of the chains.

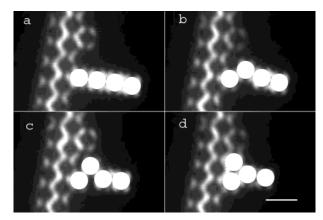
## 3. Results and Discussion

In the following, we describe the colloidal structures in the presence of magnetic fields of various strengths. Typical structures in the absence of an external magnetic field (Figure 2a) and in the presence of intermediately strong ( $H = 370 \pm 4$  A/m) (Figure 2b) and strong ( $H = 500 \pm 4$  A/m) (Figure 2c) external magentic fields are depicted in Figure 2.

3.1. Weak Chains. Figure 2a shows the colloidal arrangement in the absence of an external magnetic field. The beads are only subject to the rather weak magnetic field of the DW. This field induces magnetic moments in the beads that are sufficiently strong to lead to a dipolar attraction between the beads, thereby creating short chains (of the order of four beads), which easily undergo conformational changes. We found a distribution of final configurations of the chains after the adsorption that depends on the impact configuration when the chains first reach the DW. In Figure 2a, four different chains are marked: a threebead chain and a five-bead chain are moving toward the DW, while two four-bead chains have already adsorbed and undergone conformational changes at the DW. Note that one of the adsorbed chains has split into two fragments. The kinetics of the conformational changes of the four-bead chain in the lower part of Figure 2a is shown in Figure 3 as a function of time. In Figure 3a, the four-bead chain (highlighted in white) has just reached the interface that is loaded with two complete layers



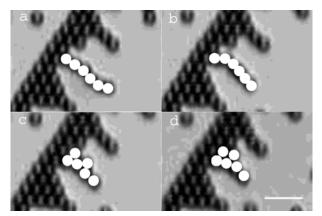
**Figure 2.** Arrangement of paramagnetic colloidal particles on top of a magnetic garnet film and close to a domain wall in the absence of an external magnetic field (taken in reflection mode) (a), in an intermediately strong magnetic field ( $H=370\pm4~\mathrm{A/m}$ ) (b), and in a strong field ( $H=500\pm4~\mathrm{A/m}$ ) (c), respectively. Pictures b and c were taken in transmission mode. The scale bars are 10 (a), 25 (b), and 20 (c)  $\mu\mathrm{m}$ , respectively.



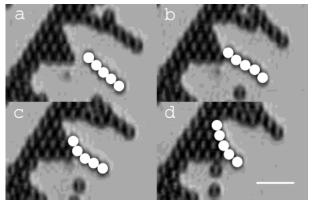
**Figure 3.** Four consecutive snapshots taken within 4 s showing the conformational changes of a four-bead chain in the absence of an external magnetic field. The scale bar is  $5 \mu m$ .

of beads. As the beads push toward the interface, the chain buckles (Figure 3b and c), allowing the second bead in the chain to attach to the interface (Figure 3d).

**3.2.** Moderately Stiff Chains. Figure 2b shows the system in an intermediately strong  $(370 \pm 4 \text{ A/m})$  magnetic field. In this situation, the beads tend to form longer (of the order of 15 beads) chains than the ones in the absence of an external field.



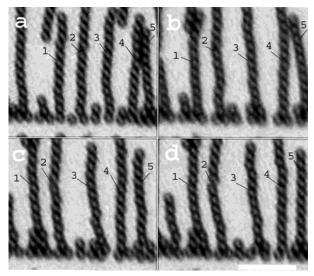
**Figure 4.** Formation of a pyramid in a magnetic field of 370  $\pm$  4 A/m. The snapshots were taken within 7 s. The scale bar is 10  $\mu$ m.



**Figure 5.** Growth of a bead pyramid upon the adsorption of a sixbead chain in a magnetic field of  $370 \pm 4$  A/m. The bead chain (highlighted) slides along a pyramid at the DW. The snapshots were taken within 8 s. The scale bar is  $10~\mu m$ .

Upon adsorption to the interface, the chains form characteristic pyramids. They have a broad base at the wall and form equilateral triangles. The typical base length is four or five beads. Their apex four to eight layers from the wall may or may not end in a chain perpendicular to the wall. In Figure 4, we show the formation of a pyramid from an adsorbing six-bead chain. The bead chains formed prior to adsorption are not only longer but also stiffer than those without a magnetic field, and they tend to keep their chain shape when attaching to the interface. Figure 5 shows the growth of a previously formed pyramid. A five-bead chain reaches the pyramid and then slides along one of the slopes, thereby keeping its linear shape and enlarging the pyramid. Eventually, merging pyramids lead to completion of the next layer close to the DW.

3.3. Stiff Chains. Figure 2c shows the system in a strong  $(500 \pm 4 \text{ A/m})$  magnetic field. The beads form very long (of the order of 30 beads) and stiff chains. They resist conformational changes at the interface, remain perpendicular to the wall, and fluctuate slightly in a transversal direction. These fluctuations give rise to the permanent exchange of beads between the chains especially in the vicinity of the DW. A chain might be attached to the domain wall by a single chain, by two legs, or by a pyramid. Some of these fluctuations are illustrated in Figure 6. In Figure 6a, chains 1, 2, and 3 are all single chains and do not have any contact with other chains at the interface; chain 5 has a pyramid base. In Figure 6b, chain 1 bends slightly and gets closer to a short chain on its left, which has two one-bead legs. Chain 2 connects with a bead on the left and a two-bead chain on the right, whereas chain 3 connects to a two-



**Figure 6.** Fluctuations of chains in a strong magnetic field of 500  $\pm$  4 A/m. The four consecutive snapshots were taken within 40 s. The scale bar is 20  $\mu$ m.

bead chain on the right and, thus, gets two two-bead legs. Chains 4 and 5 separate, and chain 4 receives two new one-bead legs. In Figure 6c, chain 1 connects to the short chain on the left, thus creating a pyramid base at the interface. In Figure 6d, chain 4 gives a leg to chain 5 and chain 5 forms a pyramid base again. Unlike in the absence or in the presence of weak external magnetic fields, where the conformations of the chains change and reach a stable state, the legs here are fluctuating with time and explore the energetically accessible configuration space.

## 4. Conclusion

We visualized conformational changes of particle chains at a one-dimensional interface. By tuning the strength of the magnetic fields, we changed the stiffness of the particle chains and their conformations at the DW. We found that in the absence of an external magnetic field the chains easily undergo conformational changes, while in a stronger field they tend to keep their chain shape. In intermediate fields, the chains formed very stable pyramids. Our system therefore can serve as a simple model system for studying conformations near interfaces.

## **References and Notes**

- (1) Jardetzky, O. Biochim. Biophys. Acta 1980, 621 (2), 227.
- (2) Semenov, A. N.; BonetAvalos, J.; Johner, A.; Joanny, J. F. *Macromolecules* **1996**, 29 (6), 2179.
- (3) Cullity, B. D. Introduction to Magnetic Materials; Addison-Wesley: Reading, MA, 1972.
- (4) Kun, F.; Wen, W. J.; Pál, K. F.; Tu, K. N. Phys. Rev. E 2001, 64, 061503
  - (5) Jin, K. J.; Wen, W. J. Phys. Lett. A 2001, 286, 347.
  - (6) Promislow, J. H. E.; Gast, A. P. Langmuir 1996, 12 (17), 4095.
- (7) Wen, W. J.; Zhang, L. Y.; Sheng, P. Phys. Rev. Lett. 2000, 85, 5464.
- (8) Lefebure, S.; Ménager, C.; Cabuil, V.; Assenheimer, M.; Gallet, F.; Flament, C. J. Phys. Chem. B 1998, 102, 2733.
- (9) Lyles, B. F.; Terrot, M. S.; Hammond, P. T.; Gast, A. P. *Langmuir* **2004**, *20*, 3028.
- (10) Melle, S.; Calderon, O. G.; Rubio, M. A.; Fuller, G. G. *Int. J. Mod. Phys. B* **2002**, *16* (17–18), 2293.
  - (11) Tlusty, T.; Safran, S. A. Science 2000, 290, 1328.
- (12) Climent, E.; Maxey, M. R.; Karniadakis, G. E. Langmuir 2004, 20, 507.
- (13) Casoli, A.; Schönhoff, M. Biol. Chem. 2001, 382 (3), 363-369.
- (14) Helseth, L. E.; Wen, H. Z.; Fischer, T. M.; Johansen, T. H. *Phys. Rev. E* **2003**, *68*, 011402.
- (15) Helseth, L. E.; Fischer, T. M.; Johansen, T. H. *Phys. Rev. Lett.* **2003**, *91*, 208302.